United States Court of Appeals

for the Second Circuit

APPENDIX

No. 74-2413

To be argued by WALTER D. AMES

IN THE

UNITED STATES COURT OF APPEALS

FOR THE SECOND CIRCUIT

MOORE BUSINESS FORMS, INC.,

Plaintiff-Appellant,

v.

MINNESOTA MINING AND MANUFACTURING COMPANY,

Defendant-Appellee.

APPEAL FROM THE UNITED STATES DISTRICT COURT
FOR THE WESTERN DISTRICT OF NEW YORK
(Honorable John T. Curtin, District Judge)

EXHIBIT TO JOINT APPENDIX

UNITED STATES COURT OF APPEALS
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EXHIBIT TO JOINT APPENDIX

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Jan. 9, 1962 N. MACAULAY 3,016,308

RECORDING PAPER COATED WITH MICROSCOPIC CAPSULES OF COLORING MATERIAL, CAPSULES AND METHOD OF MAKING

Filed Aug. 6, 1957 2 Sheets-Sheet 1

FIG. 1

MAGNIFIED CROSS-SECTION OF DISCRETE CAPSULE ACCORDING TO THE INVENTION

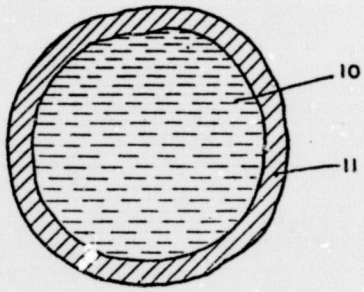
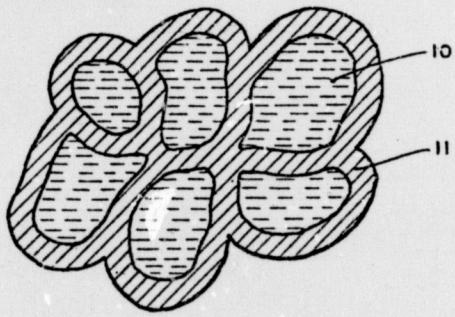


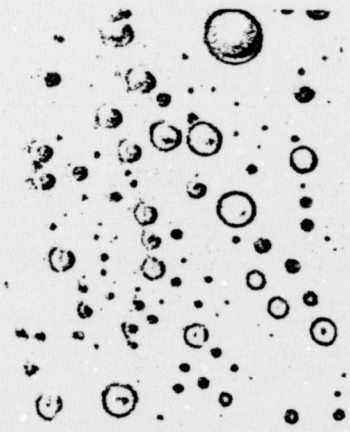
FIG. 2

MAGNIFIED CROSS-SECTION OF A CLUSTER OF DISCRETE CAPSULES ACCORDING TO THE INVENTION



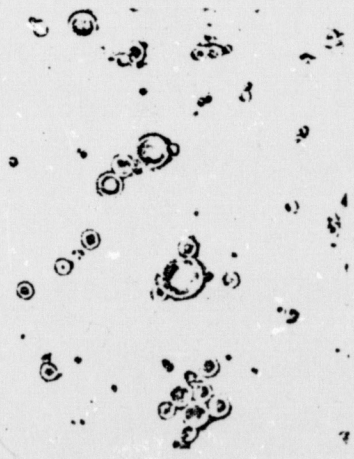
Jan. 9, 1962 N. MACAULAY 3,016,308
RECORDING PAPER COATED WITH MICROSCOPIC CAPSULES OF COLORING MATERIAL. CAPSULES AND METHOD OF MAKING
Filed Aug. 6, 1957 2 Sheets-Sheet 2

FIG. 3



PHOTOMICROGRAPH MAGNIFIED 1,000 TIMES OF DISCRETE CAPSULES ACCORDING TO THE INVENTION

FIG. 4



PHOTOMICROGRAPH MAGNIFIED 1,000 TIMES OF DISCRETE CAPSULES ACCORDING TO THE INVENTION

United States Patent Office 3,016,308 Patented Jan. 9, 1962

3,016,308

RECORDING PAPER COATED WITH MICROSCOPIC CAPSULES OF COLORING MATERIAL, CAPSULES AND METHOD OF MAKING

Norman Macaulay, Niagara Falls, N.Y., assignor to Moore Business Forms, Inc., Niagara Falls, N.Y., a corporation of Delaware

Filed Aug. 6, 1957, Ser. No. 676,574
29 Claims. (Cl. 117—36.7)

This invention relates to a novel product comprising a substantially dry free-flowing powder of microscopic discrete capsules, to the process of producing said product, and to a pressure-sensitive record or copying material having a transfer coating of said microscopic discrete capsules on at least a portion of one surface thereof. The discrete capsules which make up the free-flowing powder of the invention possess a shell or wall containing therein a marking fluid.

Present pressure-sensitive copying systems are primarily of two types. One such system employs as a coating a mixture consisting of waxes, oils, carbon black and fillers which are applied to a sheet surface as a hot melt. This type of coating, which is typified by ordinary carbon paper, provides a mark under pressure by transfer at the areas of pressure of a complete mass of coating containing the carbon black or other pigment. This waxy mixture is relatively soft and of low tensile strength and is, therefore, not resistant to scuff or offset. The mark obtained on the copy sheet is also prone to smudge and offset onto hands and clothing.

A second type of pressure sensitive copying system employs, on one side of a sheet, a continuous coating containing marking fluid inclusions. This type of system illustrates previous efforts employing minute droplets of a marking fluid in a transfer coating to be used with record material, particularly with record material in manifold form. Typical of this type of product are the record or copying materials disclosed in British Patent 392,220 and U.S. Patents Nos. 2,374,862; 2,548,366 and 2,550,466. In accordance with these patents, the paper of the record material is coated on one surface with a continuous film containing minute droplets of an oily marking fluid. In this type of copying sheet, the marking fluid may be colored or it may be colorless but capable of forming a color by a chemical reaction with another chemical upon being brought into contact with each other. Under the pressure of writing or typing, the coating ruptures and the droplets of marking fluid exude on to the copy sheet to make a mark by direct coloration or color transfer or by forming a color by chemical reaction with a coreacting chemical on the adjacent surface of the copy sheet. The difficulty with products of this type is that the surface of the coated sheet is susceptible to scuffing, abrasion and incidental rubbing which unavoidably causes rupture of the film, release of the marking fluid, and consequently smudge or offset or both. Also, on storage of the sheets, the coating material tends to dry out and crack, particularly when bended or folded, thus releasing the marking fluid through the resulting cracks to smudge or offset an adjacent copy sheet or the hands or clothing. In the case of such coatings containing a colorless marking fluid, this difficulty arises only when the ruptured film is in contact with a copy sheet or other source of the [illegible] chemical. But this is a very real disadvantage since such copying materials are not only used, but usually stored, in this condition.

Further work has been carried out in an attempt to overcome some of the objectionable features of the coatings employing fluid inclusions described hereinabove. An example of such work is described in Green Patent No. 2,712,507. According to this patent a coating for

pressure-sensitive copying materials is prepared in which the fluid inclusions of marking materials are produced having a wall about them which is somewhat more concentrated with respect to colloid solids than the remainder of the continuous dried coating on the surface of the paper. This product is predicated upon the theory that the walls about the fluid inclusions are tougher than the remainder of the colloid coating material, thus cracks which develop in the coating are said to be more prone to run between the fluid inclusions than through them and the leakage of marking fluid is said to be reduced. This type of coating requires that the walls of the fluid inclusions be of the same hydrophilic colloid material as the coating on the paper in which the fluid inclusions are dispersed, since the patent produces the fluid inclusions in the same aqueous system which is applied to paper and dried to form the continuous coating. This type of product suffers from several disadvantages. First of all, as stated above, it usually employs an aqueous coating system in which the hydrophilic colloid forming the walls about the fluid inclusions is the same as that of the continuous coating on the paper. This leads to lack of flexibility and versatility in control of the product and in coating operations. It requires that aqueous coating methods be employed. This is a serious disadvantage since aqueous coatings require that special grades of generally more expensive paper be employed and even then often results in buckling, distortion, warping of the paper since water tends to strike through or penetrate the paper. Additionally, aqueous coatings are generally not suitable for spot application or application to limited areas of one side of a sheet of paper. They are generally suitable only for application to the entire side of a sheet to produce a continuous coating.

The above disadvantages are particularly serious since in producing manifold business forms, the coating of marking material is usually applied to the backs of the sheets of paper or web. Even when a colorless color-forming dye intermediate is employed as the marking material it is generally applied to the backs of the sheets so as to react with a coreactant or developing agent which is applied to the fronts of the sheets of a manifold when pressure is applied to the sheets. During the usual handling which such business forms must undergo in their assembly, cutting, perforation, etc., the coating on the backs of the sheets containing marking fluid is in contact with the fronts of the copy sheets, which may or may not have the developing agent. When the coating on the backs of the sheets is continuous, the passage of the sheets over mill rolls, punching of holes, perforation and guillotining of edges will produce smudging or offset at areas of pressure. This undesirable smudging and offset can be minimized by spot coating the coating material on limited areas which are less subject to unavoidable mechanical pressure until actually used to produce copying.

It is an object of the present invention to provide a substantially dry free-flowing powder of microscopic discrete capsules of marking fluid which may be applied to paper and other web material to provide pressure-sensitive materials which avoid the disadvantages of the prior art.

It is another object of this invention to provide a substantially dry free-flowing powder of microscopic discrete capsules of marking fluid which may be applied to paper in a variety of ways and which does not require an aqueous coating system in preparing a pressure-sensitive copying material from the capsules.

It is a further object of this invention to provide a process for producing the substantially dry free-flowing powder of microscopic discrete capsules having an outer shell of a material which is a non-ionizable water-soluble

film-former or a hydrophobic water-insoluble film-former according to the invention.

It is an additional object of this invention to provide a superior pressure-sensitive copying or record material having the microscopic discrete capsules of marking fluid applied to at least a portion of one side of a sheet of paper or other web material.

It is also an object of this invention to provide a superior pressure-sensitive copying or record material having the microscopic discrete capsules of marking fluid applied to at least a portion of at least one side of a sheet of paper by means of a carrier or binder which is of a different material from that of the walls of the capsules.

The above enumerated objects, as well as other objects, together with the advantages of the invention, will be readily comprehended by persons skilled in the art upon reference to the following description, taken in conjunction with the annexed drawings.

In the drawings:

FIG. 1 is a greatly magnified cross-section of a discrete capsule making up the free-flowing powder according to the invention in which 10 is the marking fluid and 11 is the wall of the capsule;

FIG. 2 is a greatly magnified cross-section of a cluster of discrete capsules which is frequently produced in accordance with this invention, in which the reference numerals have the same significance as in FIG. 1;

FIG. 3 is a photomicrograph magnified 1000 times of the discrete capsules of marking fluid making up the free-flowing powder of the invention; and

FIG. 4 is a photomicrograph magnified 1000 times of another sample of discrete capsules of marking fluid making up the free-flowing powder of the invention.

The free-flowing powder of microscopic discrete capsules of the invention containing a marking fluid comprises a capsule shell or film containing a marking fluid. In FIG. 1 of the drawings, the shell is indicated at 11 and the liquid inclusion of marking fluid is shown at 10. Frequently the discrete capsules are produced in the form of aggregates or clusters as shown in FIG. 2. While FIG. 2 illustrates a cluster of six discrete capsules, the number of capsules or spheres in a cluster is usually not so great. The shell or film of the capsules is of a non-permeable nature and comprises a substance which is substantially insoluble in the liquid of the marking fluid. The capsule shell remains intact and retains the fluid within. Under substantial pressures, such as that of a pencil, pen or typewriter key, the shell will break and release the marking fluid which then marks or stains any receptive or copy material with which it comes in contact. The marking fluid may contain a colored substance which produces a direct transfer to a copy sheet or which may be an uncolored color-forming dye intermediate which reacts with a coreactant present on the copy sheet to produce a color transfer. When the microscopic discrete capsules of the invention are affixed over at least a portion of a surface, such as a surface of a sheet of paper, the coated sheet then acts as a pressure-sensitive copying material at the coated area.

The size of the microscopic capsules is desirably such that they may be dispersed in any of the common media used as binders or coatings or other backing material for application to paper without producing a surface rough to the touch. These micro-capsules may be considered as being analogous to pigment particles and they can be dispersed in any binder/vehicle combination in a manner similar to ordinary pigments. Various binder systems may be employed such as aqueous binders, an organic solvent/binder system, a plastisol or organosol binder system, a hot melt coating system or an ink-type coating which may be "set" to the paper by absorption, oxidation, evaporation, heat or moisture.

The discrete microscopic capsules of the invention are desirably of from between about 0.1 and 70 microns in diameter. More desirably, the diameter of the capsules is from about 0.5 to 20 microns. For preferred results, it has been found that a capsule diameter of between about 1 and 5 microns is most satisfactory. When the particle size exceeds 20 microns in diameter, a coating of the capsules on a paper surface may feel slightly rough to the touch. Below a diameter of one micron, the capsules are less sensitive to rupture when subjected to the pressure employed to produce copying through rupture of the capsule shell. Since it is desired to employ the microscopic capsules of the invention in pressure-sensitive copying systems which do not require the use of excessive pressures, it is desirable to provide capsules having a diameter of from about 1 to 5 microns. The microscopic capsules of the invention falling within the various particle size ranges described hereinabove exist as a free-flowing powder.

It has been found that one convenient shell thickness is approximately $\frac{1}{10}$ to $\frac{1}{5}$ of the diameter of the capsules. When shell thicknesses substantially in excess of $\frac{1}{5}$ of the diameter are produced, it has been found that the capsules are more difficult to rupture and the ability to produce a copy is reduced. With shell thicknesses substantially less than $\frac{1}{10}$ of the diameter, it has been found that the capsules are more prone to rupture prematurely and thus smudge or offset in a normal handling and preparation of the paper product. As will be appreciated by those skilled in the art, the sensitivity to rupture under pressure is dependent upon the size of the capsule as well as the thickness of the wall, with the larger size capsules having greater tendency to rupture when subjected to pressure than the smaller size capsules. Generally speaking, it is desirable to employ as thin a capsule shell as is practical.

The microscopic capsules of the invention are produced by first providing a stable emulsion having as a continuous phase the film-former material which is capable of forming the shell of the capsule. The discontinuous phase of the emulsion shall constitute the marking fluid which comprises the pigment, colored dye or colorless color-forming dye intermediate suspended or dissolved in a non-volatile liquid. An essential characteristic of a film-forming substance is that it be substantially insoluble in the marking fluid. The emulsions are produced by placing the two mutually insoluble liquids in a blender or emulsifier and by agitation producing a stable emulsion with droplets of marking fluid of the desired particle size, preferably 1 to 5 microns in diameter. The resulting emulsion is then dried, preferably by spray drying, or the continuous film-forming material first condensed around the emulsified droplets by curing or other means and then spray dried. The resulting product is a dry free-flowing powder.

The discrete microscopic capsules may be prepared by several types of emulsification processes. For example, one process which produces microscopic capsules of approximately one micron diameter is as follows: About 20 parts by weight of a non-volatile liquid containing up to 25% by weight of a pigment, colored or colorless color-forming dye intermediate is emulsified into a solution containing from about 5 to 40 or 50 parts of a film-forming material by agitation in a high-speed blender. In other words, the liquid droplets shall preferably comprise between about 23% and 80% by weight of the capsules. When the particle size of the marking fluid is substantially uniform and of the desired diameter, the resulting emulsion is sprayed into a drying chamber or spray drier to evaporate the solvent of the film-forming material. Upon drying, the film-former produces a shell about the non-volatile marking fluid. The dry free-flowing powder so produced is collected by means of a cyclone chamber and, if necessary, washed with a solvent capable of removing any marking fluid which may exist on the shell of the capsule. After washing, the powder is air dried and stored ready for use.

Another capsule-forming process employing a hot melt procedure which might be employed is as follows: About 50 parts by weight of a non-volatile liquid containing up to about 25% by weight of a pigment, colored or colorless color-forming dye intermediate is emulsified into about 50 parts by weight of a molten 100% solids film-former composition. The emulsion is produced in a high-speed agitator as in the above procedure. When the particles of color-forming marking fluid are of satisfactory particles size, the resulting emulsion is hot sprayed into a chilled chamber and the resulting solidified free-flowing powder of discrete microscopic capsules is collected.

A third process for producing the microscopic capsules in accordance with the invention employs plastisol or organosol sphere formation. The general procedure is as follows: Up to about 50 parts by weight of a non-volatile liquid containing up to about 25% by weight of pigment or colored or colorless color-forming dye intermediate is emulsified into 50 parts by weight of a dispersion of a polymeric material in a plasticizer. The dispersion employed may contain up to about 30% of a volatile diluent. The emulsion is produced by a high-speed agitator, as in the foregoing procedures, and is sprayed into a hot air chamber or spray drier where the individual particles produced are heated to a temperature such that the resin-plasticizer, film-forming combination mutually dissolves and cures to provide a rigid shell around the marking fluid particles. This resulting powder is then collected.

The shell 11 of the microscopic capsules of the invention is produced from a film-former which may be organic or inorganic in nature, capable of providing interactive forces such as are capable of producing a network in the form of a continuous dry film or shell. The film-former must be substantially insoluble in the marking fluid employed, and when the shell is produced it must not permit permeation of the marking fluid. The shell formed may be hard and brittle or, if desired, made soft and flexible by the incorporation of a plasticizer. The film-forming materials may be either of the non-ionizable water-soluble type or the hydrophobic water-insoluble (organic solvent-soluble) type. Among the film-formers which may be employed to produce the shell of the capsules are the following: acrylate and methacrylate resins, such as polymethylmethacrylate and polyacrylic acid, alkyd resins, such as those produced from esters of ethylene glycol and terephthalic acid; animal glues; casein; cellulose derivatives, such as hydroethyl cellulose, carboxymethyl cellulose, methyl cellulose, cellulose acetate, cellulose acetate butyrate and nitrocellulose; a coumarone-indene resin; furan resins, such as those of furfuraldehyde and acetophenone; petroleum hydrocarbon polymer resins, such as the "Piccopale" resins; isobutylene resins, such as polyisobutylene; isocyanate resins, such as polymers of polyesters and tolylene diisocyanate; melamine resins, such as melamine-formaldehyde; phenolic resins, such as phenol-formaldehyde resins, etc.; polyamide resins, such as alkoxy substituted nylon; rubbers, both natural and synthetic, GR–S, etc.; shellac; styrene resins, such as polystyrene, styrene-divinyl-benzene and styrene-divinyl sulfide; terpene resins, such as polyterpene; urea resins, such as urea-formaldehyde resins and urea-acetaldehyde resins; vinyl resins, such as polyvinyl chloride and polyvinyl acetate; vinylidene resins, such as vinylidine chloride-vinyl chloride ("Saran"); natural and synthetic waxes, such as paraffin and candelilla wax; and zein. Additionally, inorganic film-formers, such as sodium silicate, may be employed, although this film-former is less desirable because it is more difficult to emulsify.

The film-formers may be used alone or in combinations, where compatible, or with various plasticizers and modifying agents which impart improved characteristics, such as flexibility, scuff resistance, solvent impermeability, or,

in the case of water soluble film-formers, agents which cause water impermeability to the film-former. As an example of the latter type of material, formaldehyde may be employed to harden the shell of the capsule produced from a water-soluble film-former. A plasticizer may be one of many types of materials which modify a particular film or shell to give suitable elasticity, flexibility and toughness, etc. Among some of the satisfactory plasticizers which may be employed are: adipic acid esters, such as dioctyl adipate and dibutyl adipate; biphenyl derivatives, such as chlorinated biphenyl; glycol derivatives, such as polyethylene glycol of molecular weight of 200 to 20,000, polypropylene glycols, ethylene glycol dibutyrate and ethyl phthalyl ethyl glycolate; hydrocarbons, such as the poly-aromatic hydrocarbon oils; acid esters and ethers, such as butyl or isooctyl esters and glycol ethers of lauric, oleic, citric, abietic, adipic, azelaic, benzoic, palmitic, phosphoric acids, etc.; phthalic acid derivatives, such as dimethyl-, diethyl-, dibutyl-phthalates; polyesters, such as Flexol R–2H of Carbide and Carbon Co.; sulphonic acid derivatives, such as n-ethyl-, o-, p-toluene-sulphonamides; tall oil derivatives, such as the methyl esters of tall oil, etc.

The marking fluid may comprise any liquid, whether organic or inorganic which will provide a suspending or dissolving medium for the pigment, or colored or colorless color-forming dye intermediates. Desirably, the fluid medium within the capsule shell shall have a low volatility, i.e., wherein less than about 10% of the liquid evaporates through the shell wall over a period of several years of normal storage. Fluids having vapor pressure of less than 0.01 mm. of mercury at 25° C. are particularly satisfactory in this respect. Additionally, the fluid shall desirably have a low freezing point, i.e., a freezing point of less than 0° F., preferably as low as −30° F. Also, the fluid shall desirably have a high boiling point which will provide reduced volatility at temperatures of use. Fluids having boiling points in excess of 100° C. are usually suitable in this respect. An additional important property of the fluid is that it have a flash point above the temperature of proposed use. Fluids having a flash point above 100° C. are generally satisfactory. As those skilled in the art will appreciate, the product will be more useful, permanent and safe with liquids having higher boiling points and flash points and lower volatility and freezing points. Of course, the fluid must not dissolve the film-former or shell of the capsules. Among the satisfactory fluids which may be employed are those listed below in Table 1:

TABLE 1

Compound	V.P., mm. Hg. at 20° C.	Freezing Point, °C.	Boiling Point, °C. at 760 mm. Hg.	Flash Point, °F.
100 Sec. mineral oil				
polyethylene glycol (mol. wt. 400)		4–8		435
diethylene glycol	<0.01	−8.0	243.8	290
dipropylene glycol	0.01		231.8	280
thiodiethylene glycol	<0.01	−10.0	282.0	320
pentanediol-1,5	<0.01	−15.6	242.5	265
monoamylnaphthalene	0.01		>279	253
dibutyl maleate	<0.01	−85	280.6	285
di (2-ethyl hexyl) maleate	<0.01	−60	209 (10 mm.)	365
ethoxytriglycol	<0.01	−18.7	255.8	275
dioctyl phthalate	1.3 (200° C.)	−46	231 (5 mm.)	425
chlorinated biphenyl (Arochlor 1248 Monsanto)		<−7	340	379
methyl phthalyl ethyl glycollate	<0.01	<−35	189 (5 mm.)	374
dibutyl phthalate		−35	340	338
cottonseed oil				532
rapeseed oil		−10		530

As will be appreciated, the free-flowing powders in accordance with this invention permit extreme flexibility in the choice of film-formers and marking fluids.

The marking fluid may contain a colored pigment or

dye or it may contain a colorless color-forming dye intermediate which will react with a coreactant when brought into contact with it to produce a colored finish. The line of demarcation between pigments and dyes is often difficult to delineate. As used herein, a pigment is considered to be a colored or color-forming substance which is insoluble in the fluid of the marking fluid. Examples of pigments which may be employed are: carbon blacks, iron blues, phthalocyanines, cadmium reds, ultramarine blues, phospho- and molybdotungstic acid laked colors. A dye or dye former is herein considered to be colored or color-forming compound soluble in the fluid of the marking fluid. Among the dyes and dye formers which may be employed are: triphenylmethane, e.g., malachite green and crystal violet, azo dyes, diazonium salts, indigoid dyes, phthalocyanine dyes, anthraquinone dyes, acridine dyes, azine dyes, oxazine dyes, thiazine dyes and thioindigoid dyes.

One type of colorless color-forming dye system which may be advantageously used in the products of the invention is that described in British Patent No. 757,136. In accordance with that patent a colorless color-forming dye intermediate, such as an ether of a triphenylmethane dye former is maintained in an alkaline condition by neutralizing the dye former with an alkaline substance, in which form the dye former is colorless, and then producing a color by bringing the alkaline colorless dyestuff into contact with an excess of an acid which converts the dye former into a colored product. Among the colorless ethers of triphenylmethane dyestuffs which may be employed are the butyl ethers of methyl violet 2B, methyl violet 10B, magenta, malachite green A. In accordance with one embodiment of the present invention the marking fluid of the microscopic capsules may contain the colorless color-forming dye intermediate along with a small amount of an alkaline substance such as sodium carbonate, potassium hydroxide, etc. These capsules are applied to one surface of sheets of paper. On the opposite side of some sheets of paper is placed sufficient acid which when brought into contact with marking fluid containing the colorless color-forming dye intermediate will neutralize the dye intermediate thereby producing a color. Among the acids which may be employed to coat the opposite surface of the sheets are tannic acid, gallic acid and stearic acid. Also one may employ an acidic clay such as attapulgite clay. As will be apparent to those skilled in the art from the teachings of this disclosure, it is possible to incorporate the acid into the marking fluid of the discrete capsules and to place the colorless color-forming dye intermediate on the opposite sides of the sheets of paper. In either instance when pressure is exerted through two or more sheets in a manifold, rupture of the capsules will produce intermixing of the reacting chemicals to produce a color or copy at the sites where pressure is applied.

A coating of capsules and binder weighing 1 to 6 lbs., and preferably 2 lbs., per 500 sheets of 20" x 30" paper in which 50 to 95% of the weight of the coating consists of capsules has been found to be satisfactory.

Among the important advantages of the free-flowing capsule powders of the invention is the extreme flexibility and versatility in the manner in which they may be applied to web material, such as paper, to provide a pressure sensitive copying material having a coating of the rupturable capsules according to the invention which permits copying. What is also important is that the free-flowing capsule powders may be applied to a surface of a sheet of paper by means of a binder material which provides adhesion of the capsules to the paper surface, which binder is of a different material and different type of substance from that of the shells of the capsules. Also, binder coatings of various thickness may be employed, permitting precise control over the thickness of the coating on the paper. In essence the binder employed need serve only as an adhesive to hold the capsules to the paper. Only a small thin layer of binder is needed rather than a thick coating covering the capsules. Both aqueous binders and non-aqueous binders may be employed. Since non-aqueous binders may be used, it is not necessary to employ expensive papers thereby providing additional economies as well as a superior product. One of the particular advantages of the free-flowing powders of the invention is that it may be employed with a hot melt wax binder or dispersed in a printing ink vehicle. In the case of printing ink vehicles, the microscopic capsules may be dispersed in them and the resulting product reverse printed on a paper sheet at the same time as ordinary line printing is done. This is particularly satisfactory since it provides an excellent means of spot application whereby prescribed areas on the backs or fronts of the sheets of paper may be coated with capsules. This is one of the particular advantages of the present invention since it permits application of a transfer film or coating of capsules to only those areas of the paper where it is desired.

In order that the present invention may be better understood, the following examples of products prepared according to the invention are given for purposes of illustration. Although the number of film-formers, marking fluids, coloring and color-forming materials and binders is so great, and the number of combinations of materials suitable for making the capsules and record materials containing the capsules over an area thereof is vast, those skilled in the art will be able to readily practice the invention from reading the examples which illustrate the preparation of the products of the invention. Portions of components are given in terms of parts by weight, unless otherwise specified.

Example I

This example describes the preparation of microscopic capsules prepared by spray drying an emulsion of mineral oil in aqueous hydroxyethylcellulose.

About 30 parts of 100 second mineral oil containing 4.5 parts of Mogul A (Godfrey Cabot, Inc.) carbon black (high volatile content—low oil absorption—336 Angstrom units mean diameter) was emulsified into 700 parts of a 10% aqueous solution of hydroxyethylcellulose (having a viscosity of 250–350 centipoises at 20° C. when in the form of a 5% aqueous solution). Emulsification was accomplished by agitating the 10% aqueous solution of hydroxyethylcellulose by itself in a Waring Blendor and then pouring in the oil solution slowly while agitation was continued. A fine particle size (one micron) stable emulsion was thus produced. The resulting emulsion was injected via a fine air feed nozzle into a heated spray drying chamber of a temperature of between about 225–265° F. and the dried product collected. On examination, microscopic capsules ranging from 1 to 10 microns were observed. The capsules exuded black oil when subjected to ordinary writing pressure.

Example II

This example describes the preparation of microscopic capsules prepared by spray drying an emulsion of mineral oil in aqueous hydroxyethylcellulose.

About 17 parts of 100 second mineral oil containing 5% by weight of the butyl ether of malachite green A was emulsified into 3000 parts of a 5% aqueous solution of Cellosize WP-40 (hydroxyethylcellulose which when in the form of a 2% aqueous solution at 20° C. possesses a viscosity of 75 to 125 centipoises). An emulsion was produced and then spray dried in accordance with the procedure of Example I. A free-flowing powder of microscopic capsules was obtained.

Example III

This example describes the preparation of microscopic capsules containing a marking fluid containing a colorless color-forming dye intermediate.

About 4.5 parts of the butyl ether of methyl violet

was dissolved in 180 parts of an equal part mixture of Arochlor 1254 (a chlorinated diphenyl having a Saybolt viscosity of 44–48 seconds at 210° F.), amyl diphenyl and amylnaphthalene. The resulting solution was colorless. This solution was emulsified into 600 parts of a 10% aqueous solution by hydroxyethylcellulose in accordance with the procedure of Example I and the resulting emulsion spray dried in accordance with Example I. A free-flowing powder of microscopic capsules having particle sizes from about 0.5 to 10 microns diameter was obtained.

When the capsules were subjected to pressure they exuded colorless marking fluid which produced a strong color when absorbed on a paper impregnated with a surface of attapulgite clay or a paper surface coated with tannic acid.

Example IV

This example describes the preparation of microscopic capsules containing carbon black.

About 150 parts of a 10% Arochlor 1248 (a chlorinated diphenyl having a Saybolt viscosity of 36–37 seconds at 210° F.) and 90% 100 second mineral oil mixture containing 22.5 parts of carbon black was emulsified into 75 parts of an aqueous solution of water soluble urea-formaldehyde resin (Uformite 400–67% solids) and 2.5 parts of extra low viscosity (5–25 centipoises in a 2% aqueous solution at 25° C.) carboxymethylcellulose in 175 parts of water. The emulsion was produced in accordance with the procedure of Example I and diluted with 600 parts of water, and while continuing the rapid agitation, sufficient concentrated hydrochloric acid was added to produce condensation and precipitation of the urea formaldehyde resin. The resulting mixture was agitated for another five minutes, filtered, and the filter cake washed with water and acetone and then agitated with toluene to remove any free oily liquid. The mixture was again filtered and the filter cake air dried and then subjected to further drying at 105° C. Under microscopic examination the resulting dry, free-flowing powder was found to consist of agglomerated microscopic capsules ranging in diameter from between about 4 to 50 microns. On applying pressure to these capsules, the walls ruptured and black oil was exuded in copious quantities.

Example V

This example describes the preparation of microscopic capsules prepared from an emulsion of mineral oil in cellulose acetate.

About 100 parts of 100 second mineral oil containing about 25% by weight of nigrosine dye was emulsified into a solution of 50 parts of cellulose acetate in 600 parts of acetone in accordance with the procedure of Example I. The resulting emulsion was sprayed through an aspirator into the air to evaporate the acetone and the resulting dry microscopic capsules collected. The capsules were of about 50 micron diameter particle size. When this free-flowing powder of capsules was subjected to writing pressure, the cellulose acetate shells of the capsules were ruptured and the oil containing the nigrosine exuded therefrom in copious quantities.

Example VI

About 171 parts of 100 second mineral oil containing about 15% by weight of Du Pont Oil Blue A was emulsified in accordance with the procedure of Example I into an aqueous solution of 57 parts of hydroxyethylcellulose (which in the form of a 5% aqueous solution at 20° C. had a viscosity of 50–150 centipoises) in 570 parts of water. The resulting emulsion was spray dried to provide a free-flowing powder of capsules having a diameter of between about 1 and 5 microns. The capsules exuded the blue colored fluid when subjected to pressure to give a blue mark on a receptive surface.

Example VII

This example describes the preparation of capsules containing a colorless color-forming dye intermediate.

About 50 parts of 100 second mineral oil containing about 2 parts of the butyl ether of malachite green A (Color Index No. 657) in the alkaline condition was emulsified into a solution of 40 parts of zein and 1 part of sodium hydroxide in 200 parts of methanol. The emulsification was accomplished in accordance with the procedure of Example I. The resulting emulsion was spray dried by atomizing the emulsion into the air to provide micro-capsules ranging in size from about 1 to 60 microns. When the resulting capsules were coated to a sheet of paper and the sheet of paper placed in contact with the surface of an adjacent sheet which was coated with tannic acid, and pressure applied to the sheets in the form of pencil writing, a strongly colored mark was produced on the surface of the sheet containing the tannic acid.

Example VIII

Microscopic capsules produced in accordance with Example III to the extent of 30 parts of free-flowing capsule powder was placed into 70 parts of a 5% solution of Du Pont isobutyl methacrylate in benzene. The resulting dispersion was applied to the backs of sheets of bond paper with a doctor blade and then subsequently air dried. The fronts of these sheets of paper had been sensitized with attapulgite clay. When a manifold of sheets were stacked one above the other, with the capsule coated surfaces adjacent to the clay sensitized surfaces and writing pressure applied, a copy was produced on the fronts sensitized with clay at the sites where pressure was applied.

Example IX

Microscopic capsules produced in accordance with Example VII were placed in a flexographic vehicle (Bensing Bros. and Deeney D-536) (a water soluble protein dissolved in water) to the extent of 30 parts by weight of capsules and 70 parts of flexographic vehicle, to provide a printable ink which was applied to portions of a surface of sheets of paper by means of a gravure roll which printed the desired portion of the surface of the sheets of paper with the capsule coating. The coating dried on the paper promptly. When the resulting coated sheets were assembled with the coated portions facing adjacent sheets activated with attapulgite clay and writing pressure applied against the treated surface, a strong colored mark was produced.

Example X

About 30 parts of capsules produced in accordance with Example I were mixed with 70 parts of a mixture of 6 parts of cellulose acetate and 64 parts of acetone. The resulting mixture was applied to one surface of sheets of paper by means of a doctor blade. The sheets were permitted to dry in the air. The surface of the sheets of paper coated with the capsules provided an excellent means of copying.

Example XI

About 40 parts of paraffin wax having a melting point of 135° F. and 20 parts of FT-200 petroleum wax (Fischer-Tropsch-1) were melted together at 120° C. Into the resulting molten mixture were added about 5 parts of Alpex resin (a cyclized rubber resin) and 120 parts of Schenectady ST-5115 resin and the resulting clear melt reheated to 120° C. and maintained at this temperature. About 125 parts of a solution of 5 parts of phenyl leuco auramine in 120 parts of butyl benzyl phthalate and 0.5 part of dimethylethanolamine, heated to 120° C. was added with rapid agitation to the foregoing melt in a Waring Blendor. The emulsion so formed was sprayed via a hot air stream (150° C. temperature) inlet into a chilled atmosphere and the result

ing spherical particles collected ranged in size from 1 to 60 microns. When subjected to writing pressures, these spheres ruptured and exuded the marking fluid which gave a strong blue coloration both on a paper sheet coated with attapulgite clay and on a paper sheet coated with citric acid.

As will be apparent from the foregoing examples various components of film-formers, plasticizers, marking fluids, dyes, pigments and binders may be employed. Listed below in Table 2 are some of the components which may be employed.

TABLE 2

Film Forming Resin or Polymer	Plasticizer	Resin Solvent or Dispersion Medium	Fluid For Dye or Pigment	Dye or Pigment	Binder	Binder Solvent or Dispersion Medium
Cellulose acetate	dibutyl-phthalate	acetone	mineral oil	oil soluble blue A (du Pont).	carboxymethyl-cellulose.	water.
Hydroxyethylcellulose	polyethylene glycol 400.	water	rapesced oil	carbon black	nitrocellulose	methanol.
Zein	none	water methanol alkali.	mineral oil	butyl ether of crystal violet.	casein	water.
Styrenebutadiene copolymer	do	water	chlorinated biphenyl.	malachite green lactone.	polyvinylchloride plastisol.	none.
Melamineformaldehyde	do	do	amyl biphenyl	phthalocyanine blue pigment.	methylmethacrylate.	toluene.
Polyvinylchloride	dioctyl adipate	none	polyethylene glycol 400.	crystal violet carbinol.	nitrocellulose	methanol toluene.
Polyvinyl acetate	none	water	cottonseed oil	ultramarine blue	lithovarnish	none.
Polyvinylpyrrolidone	do	do	amylnaphthalene	"Hectograph White A" du Pont.	hot melt resin	Do.
Petroleum resin	paraffin wax	none	thiodiethylene glycol.	methyl violet	starch	water.
"Piccopale" (Penna. Indus. Chemical Co.)	mineral oil					
Cyclized rubber	do	"Troluoil" (Anderson-Prichard Oil Corp.).	polyethylene glycol 400.	"Cadmium Red Lithopone Dup" Glidden.	cellulose acetate	acetone.
Polyterpene resin	paraffin wax	none	glycerol	pigment	gelatin	water.
"Piccolyte" (Penna. Indus. Chemical Co.)	mineral oil					

Example XII

An emulsion was prepared by homogenizing 100 parts of a 50–50 mixture of polyethylene glycol 400 and ethoxytriglycol containing 7 parts of Spirit Hectograph Black A (a black pigment) (General Dyestuff Co.) into a molten mixture of 50 parts of paraffin wax and 45 parts of Piccopale 100 (a petroleum hydrocarbon resin). The resulting emulsion was sprayed into a chilled atmosphere and the solidified particles containing the colored fluid collected and stored. The spheres possessed a particle size of from 1 to 60 microns.

Example XIII

About 50 parts of Geon 121 resin (polyvinyl chloride resin) was dispersed in 50 parts of dioctylphthalate as a plasticizer. Into this mixture was emulsified 50 parts of polyethylene glycol (mol. wt. 400) containing 5 parts of carbon black. The resulting emulsion was sprayed into an air chamber at a temperature of 350° F. in order to fuse the resin and plasticizer about the fluid colored particles to form capsules containing marking fluid.

Example XIV

About 80 parts of capsules produced according to Example VII were dispersed in 120 parts of a solution of 20 parts Alpex resin (a cyclized rubber resin) in 100 parts of Troluoil (a petroleum solvent prepared by straight-run overhead distillation) (Anderson-Prichard Oil Corp.). The resulting dispersion was reverse roll coated onto paper and the coating dried over rollers at 80° C. The coated paper gave a strong coloration when placed into contact with another paper coated with citric acid and both sheets subjected to ordinary writing pressures.

Example XV

About 50 parts of capsules prepared according to Example I were dispersed in 50 parts of Geon 121 resin and 50 parts of dioctylphthalate to provide a paste. The resulting paste was printed onto paper and the coating cured by passing the coated paper over rollers at 350° F. An excellent copy sheet was produced.

It will be appreciated that if more than one copy is wanted it is possible to coat the capsules of the invention on at least a portion of one side of sheets of paper and, if necessary, a reactive coating on the other side, so that by placing a pile of such sheets one upon the other and pressing upon them with a pencil or subjecting them to the blow of a typewriter key, a suitable number of copies can be obtained depending upon the amount of pressure applied and the thickness of the paper.

The terms and expressions which have been employed are used as terms of description and not of limitation, and it is not intended, in the use of such terms and expressions, to exclude any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. A process for producing a free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell being formed directly by evaporation forces on the solvent of a film-former solution of a non-ionizable water-soluble film-former which comprises the continuous phase of suspended minute particles of an emulsion, the discontinuous phase of which emulsion comprises the liquid droplets and between about 23% and 80% by weight of the capsules, which process comprises producing an emulsion of the liquid droplets in a film-former solution in which the latter forms the continuous phase and is substantially insoluble in the liquid droplets, suspending minute particles of said emulsion in a gaseous atmosphere, and then subjecting said suspended emulsion particles to evaporation forces to produce said microscopic discrete capsules in the form of a free-flowing powder.

2. A process defined by claim 1, wherein the drying is accomplished by spray evaporation.

3. A process as defined by claim 1, wherein the resulting capsules which are produced have a diameter of between about 0.1 and 70 microns.

4. A process for producing a free-flowing powder of

microscopic discrete rupturable capsules comprising marking fluid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell being formed directly by evaporation forces on the solvent of a film-former solution of a non-ionizable water-soluble film-former which comprises the continuous phase of suspended minute particles of an emulsion, the discontinuous phase of which emulsion comprises the marking fluid droplets and between about 23% and 80% by weight of the capsules, which process comprises producing an emulsion of the marking fluid in a film-former solution in which the latter forms the continuous phase and is substantially insoluble in the marking fluid, suspending minute particles of said emulsion in a gaseous atmosphere, and then subjecting said suspended minute emulsion particles to evaporation forces to produce said microscopic discrete capsules in the form of a free-flowing powder.

5. A process as defined by claim 4 wherein said marking fluid comprises a colored material.

6. A process for producing a free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell being formed from a hot molten non-aqueous film-former comprising the continuous phase of an emulsion, the discontinuous phase of which emulsion comprises liquid droplets comprising between about 23% and 80% by weight of the emulsion, which process comprises producing an emulsion of the liquid droplets in said hot molten non-aqueous film-former in which the latter forms the continuous phase and is substantially insoluble in the liquid droplets, suspending minute particles of said emulsion in a gaseous atmosphere, and cooling the suspended particles to solidify said film-former and produce microscopic discrete rupturable capsules in the form of a free-flowing powder.

7. A process as defined by claim 6, wherein the resulting capsules have a diameter between about 0.1 and 70 microns.

8. A process for producing a free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell consisting of a hydrophobic water-insoluble material produced by the chemical condensation of the reactive constituents of the film-former dissolved in aqueous solution, said solution comprising the continuous phase of an emulsion, the discontinuous phase of which emulsion comprises liquid droplets comprising between about 23% and 80% by weight of the capsules, which process comprises producing an emulsion of the liquid droplets in said aqueous solution of film-former constituents, causing said film-former constituents to undergo chemical condensation about the liquid droplets, and thereby produce said microscopic discrete rupturable capsules in the form of a free-flowing powder.

9. A process for producing a free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell being formed of a plastisol film-former comprising the continuous phase of an emulsion, the discontinuous phase of which emulsion comprises liquid droplets comprising between about 23% and 80% by weight of the capsules, which process comprises producing an emulsion of the liquid droplets in said plastisol film-former in which the latter forms the continuous phase and is substantially insoluble in the liquid droplets, heating minute particles of said emulsion to thereby produce said microscopic discrete rupturable capsules in the form of a free-flowing powder.

10. A process for producing a free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell being formed directly by evaporation forces on the organic solvent of a film-former solution of a hydrophobic water-insoluble film-former in an organic solvent which comprises the continuous phase of suspended minute particles of an emulsion, the discontinuous phase of which emulsion comprises the liquid droplets, and between about 23% and 80% by weight of the capsules, which process comprises producing an emulsion of the liquid droplets in the film-former solution in which the latter forms the continuous phase and is substantially insoluble in the liquid droplets, suspending minute particles of said emulsion in a gaseous atmosphere, and then subjecting said suspended emulsion particles to evaporation forces to produce said microscopic discrete capsules in the form of a free-flowing powder.

11. A free-flowing powder of microscopic discrete rupturable capsules having a particle size of between about 0.1 and 70 microns diameter, said capsules comprising liquid droplets encapsulated within an outer shell rupturable under pressure, said liquid droplets being substantially insoluble in and incapable of dissolving said outer shell and comprising between about 23% and 80% by weight of said capsules, said outer shell having a thickness comprising from about one-tenth to one-third of the capsule diameter and comprising a material selected from the class consisting of a non-ionizable water-soluble film-former and a hydrophobic water-insoluble film-former.

12. A substantially dry free-flowing powder as defined by claim 11 wherein the capsules have a particle size of between about 1 and 20 microns diameter.

13. A substantially dry free-flowing powder as defined by claim 11 wherein the capsules have a particle size of between about 1 and 5 microns diameter.

14. A free-flowing powder of microscopic discrete rupturable capsules as defined by claim 11 wherein the outer shell material is a non-ionizable water-soluble film-former comprising a cellulosic material.

15. A free-flowing powder of microscopic discrete rupturable capsules as defined by claim 14 wherein the liquid droplets comprise a marking fluid.

16. A free-flowing powder of microscopic discrete rupturable capsules as defined by claim 11 wherein the shell material is a hydrophobic water-insoluble film-former comprising a chemical condensation polymer.

17. A free-flowing powder of microscopic discrete rupturable capsules as defined by claim 16 wherein the liquid droplets comprise a marking fluid.

18. A free-flowing powder of microscopic discrete rupturable capsules as defined by claim 11 wherein the shell material is a hydrophobic water-insoluble film-former comprising a vinyl polymer.

19. A free-flowing powder of microscopic discrete rupturable capsules as defined by claim 18 wherein the liquid droplets comprise a marking fluid.

20. A free-flowing powder of microscopic discrete rupturable capsules as defined by claim 11 wherein the shell material comprises a fusible wax material.

21. A free-flowing powder of microscopic discrete rupturable capsules as defined by claim 20 wherein the liquid droplets comprise a marking fluid.

22. A free-flowing powder of microscopic discrete rupturable capsules as defined by claim 11 wherein the liquid droplets comprise a marking fluid.

23. A record copying sheet having on at least a portion of one side thereof a coating of a free-flowing powder of microscopic discrete capsules comprising a rupturable shell containing therein a marking fluid capable of being liberated when the shells of said discrete capsules are ruptured upon being subjected to an external printing or marking pressure, said microscopic discrete capsules being those defined by claim 11.

24. A record copying sheet having on at least a portion of one side thereof a coating of microscopic discrete capsules comprising a rupturable shell containing therein a

marking fluid capable of being liberated when the shells of said discrete capsules are ruptured upon being subjected to external pressure, said capsules being held to said sheet by a binder which is of a different substance from that forming the rupturable shell of said capsules, said microscopic discrete capsules being those defined by claim 11.

25. Paper having coated on at least a portion of a surface thereof microscopic discrete capsules comprising a rupturable shell containing therein a marking fluid capable of being liberated when the shells of said discrete capsules are ruptured upon being subjected to external pressure, said capsules being held to said sheet by a binder which is of a different substance from that forming the rupturable shell of said capsules, said microscopic discrete capsules being those defined by claim 11.

26. Paper as defined by claim 25 wherein the marking fluid comprises a colored transfer substance.

27. Paper as defined by claim 25 wherein the marking fluid comprises a colorless material forming a color when brought into contact with another substance.

28. Paper as defined by claim 25 wherein the marking fluid comprises a colorless dye-former capable of producing a color when in the presence of an acidic substance.

29. Paper as defined by claim 25 wherein the capsules have a diameter of between about 0.1 and 70 microns.

References Cited in the file of this patent

UNITED STATES PATENTS

2,650,895	Wallenmeyer	Sept. 1, 1953
2,711,375	Sandberg	June 21, 1955
2,712,507	Green	July 5, 1955
2,777,798	Hochberg	Jan. 15, 1957
2,800,457	Green	July 23, 1957
2,800,458	Green	July 23, 1957

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11

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,016,308 January 9, 1962

Norman Macaulay

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 31, for "bands" read -- hands --; column 5, line 10, for "particles" read -- particle --; line 42, for "hydropholic" read -- hydrophobic --; column 7, line 11, before "colored" insert -- a --; column 9, line 6, for "by" read -- of --; columns 11 and 12, TABLE 2", the horizontal lines beginning "Petroleum resin" and "Piccopale" should be presented as a single composition and not as two separate compositions as in the patent.

Signed and sealed this 19th day of June 1962.

(SEAL)

Attest:

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Attesting Officer

DAVID L. LADD
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APPLICATION

SERIAL NO. (Series of 1948) 676574	F.R.	PATENT NUMBER 3016308
Assistant examiner	Class / Subclass	DATED JAN-9 1962
Division No. 25	Filed complete (Date) AUG 6 1957 / Serial No. 676 574	CLAIMS FOREIGN PRIORITY: Country / Date

Applicant(s)

MACAULAY, NORMAN C. NIAGARA FALLS, N. Y.

Number claims allowed	Print claim(s)	Class	Subclass
29	1	117	

Assignor to Morse Business Forms, Inc., Niagara Falls, N. Y.
a Corp. of Delaware

Title of invention: Recording Paper Coated With Microscopic Capsules of Colorless ~~Compound~~ ~~NOVEL COLORED PRODUCTS AND PROCESS OF~~ Producing the Coated Material, Apparatus and Method of Making

☐ Division of ☐ Continuation of ☐ Substitute for abandoned APPLICATION

Sheets	Extra claims	Filing fee	Transaction	Atty's docket
2	1	$31	15043	

Serial No.	Filed	Now Patent No.	Granted

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NOTICE OF ALLOWANCE MAILED
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Date	Amount
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5.	Ltr. to Dft. June 11, 1958	30.	
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12.	Brief (3) Sept 21, 1960	37.	
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15.	Brief (3) Filed Feb 23 1961	40.	
16.	Order E. MAR 31 1961 3/23	41.	
17.	[illegible] MAR 31 1961	42.	
18.	Request for C & C May 15, 1962	43.	
19.	Communication Letter May 11, 1962	44.	
20.	Extension Letter May 15, 1962	45.	
21.	Board Jan. 25, 1972	46.	
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		48.	
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676574
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Assistant examiner

Application No.

Applicant(s)

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Class	Sub	Date	Ex'r
117	36	10-26-57	MK
117	36	11-19-57	MK
167	81 R9		
	82		
18	Cop. Div.	2-10-60	MK
	588		
167	83		
252	316		
Art Search		3-22-61	MK
117	36		
	155		
167	83		
106	20-32		
252	316		

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	59										119			
	60										120			

SYMBOLS	STATUS
V	Rejected
=	Allowed
– (Through number)	Canceled
+	Restriction requirement
N	Nonelected invention or
I	Interference
A	Appeal

B 1043

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August 5, 1957

Hon. Commissioner of Patents,

Washington 25, D. C.

Sir:

Enclosed is an application of Norman Macaulay for improvements in NOVEL MARKING PRODUCTS AND PROCESS, comprising petition, specification, oath and drawings (2 sheets), together with a check for $30 to cover the filing fee.

Respectfully,

Louis F. Reed

Attorney for Applicant

LFR:rn

Enclosures

30.00 - 101- SOLE
1.00 - 102 B 1030

676574

APPLICATION

FOR

UNITED STATES LETTERS PATENT

Specification.

TO ALL WHOM IT MAY CONCERN:

BE It Known, that I, NORMAN MACKAY, a citizen of ~~the United States~~ Great Britain residing at ~~1387 Cleveland Avenue~~, Niagara Falls, in the County of Niagara and State of New York, have invented certain new and useful improvements in NOVEL MARKING PRODUCTS AND PROCESS, of which the following is a specification:

AJ-657

AJ-657 15845

This invention relates to a novel product comprising a substantially dry free-flowing powder of microscopic discrete capsules ~~of a marking-fluid~~, to the process of producing said product, and to a pressure-sensitive record or copying material having a transfer coating of said microscopic discrete capsules on at least a portion of one surface thereof. The discrete capsules which make up the free-flowing powder of the invention possess a shell or wall containing therein a marking fluid.

Present pressure-sensitive copying systems are primarily of two types. One such system employs as a coating a mixture consisting of waxes, oils, carbon black and fillers which are applied to a sheet surface as a hot melt. This type of coating, which is typified by ordinary carbon paper, provides a mark under pressure by transfer at the areas of pressure of a complete mass of coating containing the carbon black or other pigment. This waxy mixture is relatively soft and of low tensile strength and is, therefore, not resistant to scuff or offset. The mark obtained on the copy sheet is also prone to smudge and offset onto hands and clothing.

A second type of pressure sensitive copying system employs, on one side of a sheet, a continuous coating containing marking fluid inclusions. This type of system illustrates previous efforts employing minute droplets of a marking fluid in a transfer coating to be used with record material, particularly with record material in manifold form. Typical of this type of product are the record or copying

materials disclosed in British patent 392,220 and U.S. patents Nos. 2,374,862; 2,548,366 and 2,550,466. In accordance with these patents, the paper of the record material is coated on one surface with a continuous film containing minute droplets of an oily marking fluid. In this type of copying sheet, the marking fluid may be colored or it may be colorless but capable of forming a color by a chemical reaction with another chemical upon being brought into contact with each other. Under the pressure of writing or typing, the coating ruptures and the droplets of marking fluid exude on to the copy sheet to make a mark by direct coloration or color transfer or by forming a color by chemical reaction with a coreacting chemical on the adjacent surface of the copy sheet. The difficulty with products of this type is that the surface of the coated sheet is susceptible to scuffing, abrasion and incidental rubbing which unavoidably causes rupture of the film, release of the marking fluid, and consequently smudge or offset or both. Also, on storage of the sheets, the coating material tends to dry out and crack, particularly when bended or folded, thus releasing the marking fluid through the resulting cracks to smudge or offset an adjacent copy sheet or the hands or clothing. In the case of such coatings containing a colorless marking fluid, this difficulty arises only when the ruptured film is in contact with a copy sheet or other source of the coreacting chemical. But this is a very real disadvantage since such copying materials are not only used, but usually stored, in this condition.

Further work has been carried out in an attempt to overcome some of the objectionable features of the coatings employing fluid inclusions described hereinabove. An example of such work is described in Green patent No. 2,712,507. According to this patent a coating for pressure-sensitive copying materials is prepared in which the fluid inclusions of marking materials are produced having a wall about them which is somewhat more concentrated with respect to colloid solids than the remainder of the continuous dried coating on the surface of the paper. This product is predicated upon the theory that the walls about the fluid inclusions are tougher than the remainder of the colloid coating material, thus cracks which develop in the coating are said to be more prone to run between the fluid inclusions than through them and the leakage of marking fluid is said to be reduced. This type of coating requires that the walls of the fluid inclusions be of the same hydrophilic colloid material as the coating on the paper in which the fluid inclusions are dispersed, since the patent produces the fluid inclusions in the same aqueous system which is applied to paper and dried to form the continuous coating. This type of product suffers from several disadvantages. First of all, as stated above, it usually employs an aqueous coating system in which the hydrophilic colloid forming the walls about the fluid inclusions is the same as that of the continuous coating on the paper. This leads to lack of flexibility and versatility in control of the product and in coating operations. It requires that aqueous coating

methods be employed. This is a serious disadvantage since aqueous coatings require that special grades of generally more expensive paper be employed and even then often results in buckling, distortion, warping of the paper since water tends to strike through or penetrate the paper. Additionally, aqueous coatings are generally not suitable for spot application or application to limited areas of one side of a sheet of paper. They are generally suitable only for application to the entire side of a sheet to produce a continuous coating.

The above disadvantages are particularly serious since in producing manifold business forms, the coating of marking material is usually applied to the backs of the sheets of intermediate paper or web. Even when a colorless color-forming dye is employed as the marking material it is generally applied to the backs of the sheets so as to react with a coreactant or developing agent which is applied to the fronts of the sheets of a manifold when pressure is applied to the sheets. During the usual handling which such business forms must undergo in their assembly, cutting, perforation, etc., the coating on the backs of the sheets containing marking fluid is in contact with the fronts of the copy sheets, which may or may not have the developing agent. When the coating on the backs of the sheets is continuous, the passage of the sheets over mill rolls, punching of holes, perforation and guillotining of edges will produce smudging or offset at areas of pressure. This undesirable smudging and offset can be minimized by spot coating the coating material on limited areas which are less

subject to unavoidable mechanical pressure until actually used to produce copying.

It is an object of the present invention to provide a substantially dry free-flowing powder of microscopic discrete capsules of marking fluid which may be applied to paper and other web material to provide pressure-sensitive materials which avoid the disadvantages of the prior art.

It is another object of this invention to provide a substantially dry free-flowing powder of microscopic discrete capsules of marking fluid which may be applied to paper in a variety of ways and which does not require an aqueous coating system in preparing a pressure-sensitive copying material from the capsules.

It is a further object of this invention to provide a process for producing the substantially dry free-flowing powder of microscopic discrete capsules of ~~marking fluid~~ according to the invention.

It is an additional object of this invention to provide a superior pressure-sensitive copying or record material having the microscopic discrete capsules of marking fluid applied to at least a portion of one side of a sheet of paper or other web material.

It is also an object of this invention to provide a superior pressure-sensitive copying or record material having the microscopic discrete capsules of marking fluid applied to at least a portion of at least one side of a sheet of paper by means of a carrier or binder which is of a different material from that of the walls of the capsules.

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The above enumerated objects, as well as other objects, together with the advantages of the invention, will be readily comprehended by persons skilled in the art upon reference to the following description, taken in conjunction with the annexed drawings.

In the drawings:

Fig. 1 is a greatly magnified cross-section of a discrete capsule making up the free-flowing powder according to the invention in which 10 is the marking fluid and 11 is the wall of the capsule;

Fig. 2 is a greatly magnified cross-section of a cluster of discrete capsules which is frequently produced in accordance with this invention, in which the reference numerals have the same significance as in Fig. 1;

Fig. 3 is a photomicrograph magnified 1000 times of the discrete capsules of marking fluid making up the free-flowing powder of the invention; and

Fig. 4 is a photomicrograph magnified 1000 times of another sample of discrete capsules of marking fluid making up the free-flowing powder of the invention.

The free-flowing powder of microscopic discrete capsules of the invention containing a marking fluid comprises a capsule shell or film containing a marking fluid. In Fig. 1 of the drawings, the shell is indicated at 11 and the liquid inclusion of marking fluid is shown at 10. Frequently the discrete capsules are produced in the form of aggregates or clusters as shown in Fig. 2. While Fig. 2

illustrates a cluster of six discrete capsules, the number of capsules or spheres in a cluster is usually not so great. The shell or film of the capsules is of a non-permeable nature and comprises a substance which is substantially insoluble in the liquid of the marking fluid. The capsule shell remains intact and retains the fluid within. Under substantial pressures, such as that of a pencil, pen or typewriter key, the shell will break and release the marking fluid which then marks or stains any receptive or copy material with which it comes in contact. The marking fluid may contain a colored substance which produces a direct transfer to a copy sheet or which may be an uncolored color-forming dye intermediate which reacts with a coreactant present on the copy sheet to produce a color transfer. When the microscopic discrete capsules of the invention are affixed over at least a portion of a surface, such as a surface of a sheet of paper, the coated sheet then acts as a pressure-sensitive copying material at the coated area.

The size of the microscopic capsules is desirably such that they may be dispersed in any of the common media used as binders or coatings or other backing material for application to paper without producing a surface rough to the touch. These micro-capsules may be considered as being analogous to pigment particles and they can be dispersed in any binder/vehicle combination in a manner similar to ordinary pigments. Various binder systems may be employed such as aqueous binders, an organic solvent/binder system, a plastisol

or organosol binder system, a hot melt coating system or an ink-type coating which may be set to the paper by absorption, oxidation, evaporation, heat or moisture.

The discrete microscopic capsules of the invention are desirably of from between about 0.1 and 70 microns in diameter. More desirably, the diameter of the capsules is from about 0.5 to 20 microns. For preferred results, it has been found that a capsule diameter of between about 1 and 5 microns is most satisfactory. When the particle size exceeds 20 microns in diameter, a coating of the capsules on a paper surface may feel slightly rough to the touch. Below a diameter of one micron, the capsules are less sensitive to rupture when subjected to the pressure employed to produce copying through rupture of the capsule shell. Since it is desired to employ the microscopic capsules of the invention in pressure-sensitive copying systems which do not require the use of excessive pressures, it is desirable to provide capsules having a diameter of from about 1 to 5 microns. The microscopic capsules of the invention falling within the various particle size ranges described hereinabove exist as a free-flowing powder.

It has been found that one convenient shell thickness is approximately 1/10 to 1/3 of the diameter of the capsules. When shell thicknesses substantially in excess of 1/3 of the diameter are produced, it has been found that the capsules are more difficult to rupture and the ability to produce a copy is reduced. Wall shell thicknesses substantially less

than 1/10 of the diameter, it has been found that the capsules are more prone to rupture prematurely and thus smudge or offset in a normal handling and preparation of the paper product. As will be appreciated by those skilled in the art, the sensitivity to rupture under pressure is dependent upon the size of the capsule as well as the thickness of the wall, with the larger size capsules having greater tendency to rupture when subjected to pressure than the smaller size capsules. Generally speaking, it is desirable to employ as thin a capsule shell as is practical.

The microscopic capsules of the invention are produced by first providing a stable emulsion having as a continuous phase the film-former material which is capable of forming the shell of the capsule. The discontinuous phase of the emulsion shall constitute the marking fluid which comprises the pigment, colored dye or colorless color-forming dye intermediate suspended or dissolved in a non-volatile liquid. An essential characteristic of a film-forming substance is that it be substantially insoluble in the marking fluid. The emulsions are produced by placing the two mutually insoluble liquids in a blendor or emulsifier and by agitation producing a stable emulsion with droplets of marking fluid of the desired particle size, preferably 1 to 5 microns in diameter. The resulting emulsion is then dried, preferably by spray drying, or the continuous film-forming material first condensed around the emulsified droplets by curing or other means and then spray dried. The resulting product is a dry free-flowing powder.

The discrete microscopic capsules may be prepared by several types of emulsification processes. For example, one process which produces microscopic capsules of approximately one micron diameter is as follows: About 20 parts by weight of a non-volatile liquid containing up to 25% by weight of a pigment, colored or colorless color-forming dye intermediate is emulsified into a solution containing from about 5 to 40 or 50 parts of a film-forming material by agitation in a high-speed blendor. When the particle size of the marking fluid is substantially uniform and of the desired diameter, the resulting emulsion is sprayed into a drying chamber or spray drier to evaporate the solvent of the film-forming material. Upon drying, the film-former produces a shell about the non-volatile marking fluid. The dry free-flowing powder so produced is collected by means of a cyclone chamber and, if necessary, washed with a solvent capable of removing any marking fluid which may exist on the shell of the capsule. After washing, the powder is air dried and stored ready for use.

Another capsule-forming process employing a hot melt procedure which might be employed is as follows: About 50 parts by weight of a non-volatile liquid containing up to about 25% by weight of a pigment, colored or colorless color-forming dye intermediate is emulsified into about 50 parts by weight of a molten 100% solids film-former composition. The emulsion is produced in a high-speed agitator as in the above procedure. When the particles of color-forming marking fluid are of satisfactory particle size, the resulting emulsion is hot sprayed into a

chilled chamber and the resulting solidified free-flowing powder of discrete microscopic capsules is collected.

A third process for producing the microscopic capsules in accordance with the invention employs plastisol or organosol sphere formation. The general procedure is as follows: Up to about 50 parts by weight of a non-volatile liquid containing up to about 25% by weight of pigment or colored or colorless color-forming dye intermediate is emulsified into 50 parts by weight of a dispersion of a polymeric material in a plasticizer. The dispersion employed may contain up to about 30% of a volatile diluent. The emulsion is produced by a high-speed agitator, as in the foregoing procedures, and is sprayed into a hot air chamber or spray drier where the individual particles produced are heated to a temperature such that the resin-plasticizer, film-forming combination mutually dissolves and cures to provide a rigid shell around the marking fluid particles. This resulting powder is then collected.

The shell 11 of the microscopic capsules of the invention is produced from a film-former which may be organic or inorganic in nature, capable of providing interactive forces such as are capable of producing a network in the form of a continuous dry film or shell. The film-former must be substantially insoluble in the marking fluid employed, and when the shell is produced it must not permit permeation of the marking fluid. The shell formed may be hard and brittle or, if desired, made soft and flexible by the incorporation of a plasticizer. The film-forming materials may be either of the

water-soluble type or the organic solvent-soluble type. Among the film-formers which may be employed to produce the shell of the capsules are the following: acrylate and methacrylate resins, such as polymethylmethacrylate and polyacrylic acid; alkyd resins, such as those produced from esters of ethylene glycol and terephthalic acid; animal glues; casein; cellulose derivatives, such as hydroethyl cellulose, carboxymethyl cellulose, methyl cellulose, cellulose acetate, cellulose acetate butyrate and nitrocellulose; a coumarone-indene resin; furan resins, such as those of furfuraldehyde and acetophenone; petroleum hydrocarbon polymer resins, such as the "Piccopale" resins; isobutylene resins, such as polyisobutylene; isocyanate resins, such as polymers of polyesters and tolylene diisocyanate; melamine resins, such as melamine-formaldehyde; phenolic resins, such as phenol-formaldehyde resins, etc.; polyamide resins, such as alkoxy substituted nylon; rubbers, both natural and synthetic, GR-S, etc.; shellac; styrene resins, such as polystyrene, styrene-divinylbenzene and styrene-divinyl sulfide; terpene resins, such as polyterpene; urea resins, such as urea-formaldehyde resins and urea-acetaldehyde resins; vinyl resins, such as polyvinyl chloride and polyvinyl acetate; vinylidene resins, such as vinylidine chloride — vinyl chloride ("Saran"); natural and synthetic waxes, such as paraffin and candelia wax; and zein. Additionally, inorganic film-formers, such as sodium silicate, may be employed, although this film-former is less desirable because it is more difficult to emulsify.

The film-formers may be used alone or in combinations, where compatible, or with various plasticizers and modifying agents which impart improved characteristics, such as flexibility, scuff resistance, solvent impermeability, or, in the case of water soluble film-formers, agents which cause water impermeability to the film-former. As an example of the latter type of material, formaldehyde may be employed to harden the shell of the capsule produced from a water-soluble film-former. A plasticizer may be one of many types of materials which modify a particular film or shell to give suitable elasticity, flexibility and toughness, etc. Among some of the satisfactory plasticizers which may be employed are: adipic acid esters, such as dioctyl adipate and dibutyl adipate; biphenyl derivatives, such as chlorinated biphenyl; glycol derivatives, such as polyethylene glycol of molecular weight of 200 to 20,000, polypropylene glycols, ethylene glycol dibutyrate and ethyl phthalyl ethyl glycolate; hydrocarbons, such as the polyaromatic hydrocarbon oils; acid esters and ethers, such as butyl or isooctyl esters and glycol ethers of lauric, oleic, citric, abietic, adipic, azelaic, benzoic, palmitic, phosphoric acids, etc.; phthalic acid derivatives, such as dimethyl-, diethyl-, dibutyl-phthalates; polyesters, such as Flexol R-2H of Carbide and Carbon Co.; sulphonic acid derivatives, such as n-ethyl-, o-, p-toluene-sulphonamides; tall oil derivatives, such as the methyl esters of tall oil, etc.

The marking fluid may comprise any liquid, whether organic or inorganic which will provide a suspending or dissolving medium for the pigment, or colored or colorless color-forming dye intermediates. Desirably, the fluid medium within the capsule shell shall have a low volatility, i.e., wherein less than about 10% of the liquid evaporates through the shell wall over a period of several years of normal storage. Fluids having vapor pressure of less than 0.01 mm. of mercury at 25° C. are particularly satisfactory in this respect. Additionally, the fluid shall desirably have a low freezing point, i.e., a freezing point of less than 0° F., preferably as low as -30° F. Also, the fluid shall desirably have a high boiling point which will provide reduced volatility at temperatures of use. Fluids having boiling points in excess of 100° C. are usually suitable in this respect. An additional important property of the fluid is that it have a flash point above the temperature of proposed use. Fluids having a flash point above 100° C. are generally satisfactory. As those skilled in the art will appreciate, the product will be more useful, permanent and safe with liquids having higher boiling points and flash points and lower volatility and freezing points. Of course, the fluid must not dissolve the film-former or shell of the capsules. Among the satisfactory fluids which may be employed are those listed below in Table 1:

Table 1

Compound	V.P., mm. Hg at 20° C.	Freezing Point, ° C.	Boiling Point, ° C. at 760 mm. Hg	Flash Point, ° F.
100 Sec. mineral oil				
polyethylene glycol (mol. wt. 400)	--	4-8	--	435
diethylene glycol	<0.01	-8.0	245.8	290
dipropylene glycol	0.01	--	231.8	280
thiodiethylene glycol	<0.01	-10.0	282.0	320
pentanediol -1,5	<0.01	-15.6	242.5	265
monoamylnaphthalene	0.01	--	>279	255
dibutyl malcate	<0.01	-85	280.6	285
di (2-ethyl hexyl) malcate.	<0.01	-60	209 (10 mm.)	365
ethoxytriglycol	<0.01	-18.7	255.8	275
dioctyl phthalate	1.3 (200°C.)	-40	231 (5 mm.)	425
chlorinated biphenyl (Aroclor 1248 Monsanto)	--	<-7	340	379
methyl phthalyl-ethyl glycollate	<0.01	<-35	189 (5 mm.)	374
dibutyl phthalate	--	-35	340	338
cottonseed oil	--	--	--	582
rapeseed oil	--	-10	--	530

As will be appreciated, the free-flowing powders in accordance with this invention permit extreme flexibility in the choice of film formers and marking fluids.

The marking fluid may contain a colored pigment or dye or it may contain a colorless color-forming dye intermediate which will react with a coreactant when brought into contact with it to produce a colored finish. The line of demarcation between pigments and dyes is often difficult to delineate. As used herein, a pigment is considered to be a colored or color-forming substance which is insoluble in the fluid of the marking fluid. Examples of pigments which may be employed are: carbon blacks, iron blues, phthalocyanines, cadmium reds, ultramarine blues, phospho- and molybdotungstic acid laked colors. A dye or dye former is herein considered to be a colored or color-forming compound soluble in the fluid of the marking fluid. Among the dyes and dye formers which may be employed are: triphenylmethane, e.g., malachite green and crystal violet, azo dyes, diazonium salts, indigoid dyes, phthalocyanine dyes, anthraquinone dyes, acridine dyes, azine dyes, oxazine dyes, thiazine dyes and thioindigoid dyes.

One type of colorless color-forming dye system which may be advantageously used in the products of the invention is that described in British patent No. 757,136. In accordance with that patent a colorless color-forming dye intermediate, such as an ether of a triphenylmethane dye former is maintained in an alkaline condition by neutralizing the dye former with an alkaline substance, in which form the dye former is colorless, and then producing a color by bringing the alkaline colorless dyestuff into contact with an excess of an acid which converts the dye former into a

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colored product. Among the colorless ethers of triphenylmethane dyestuffs which may be employed are the butyl ethers of methyl violet 2B, methyl violet 10B, magenta, malachite green A. In accordance with one embodiment of the present invention the marking fluid of the microscopic capsules may contain the colorless color-forming dye intermediate along with a small amount of an alkaline substance such as sodium carbonate, potassium hydroxide, etc. These capsules are applied to one surface of sheets of paper. On the opposite side of some sheets of paper is placed sufficient acid which when brought into contact with marking fluid containing the colorless color-forming dye intermediate will neutralize the dye intermediate thereby producing a color. Among the acids which may be employed to coat the opposite surface of the sheets are tannic acid, gallic acid and stearic acid. Also one may employ an acidic clay such as attapulgite clay. As will be apparent to those skilled in the art from the teachings of this disclosure, it is possible to incorporate the acid into the marking fluid of the discrete capsules and to place the colorless color-forming dye intermediate on the opposite sides of the sheets of paper. In either instance when pressure is exerted through two or more sheets in a manifold, rupture of the capsules will produce intermixing of the reacting chemicals to produce a color or copy at the sites where pressure is applied.

A coating of capsules and binder weighing 1 to 6 lbs., and preferably 2 lbs., per 500 sheets of 20" x 30" paper in which 50 to 95% of the weight of the coating consists of capsules has been found to be satisfactory.

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Among the important advantages of the free-flowing capsule powders of the invention is the extreme flexibility and versatility in the manner in which they may be applied to web material, such as paper, to provide a pressure sensitive copying material having a coating of the rupturable capsules according to the invention which permits copying. What is also important is that the free-flowing capsule powders may be applied to a surface of a sheet of paper by means of a binder material which provides adhesion of the capsules to the paper surface, which binder is of a different material and different type of substance from that of the shells of the capsules. Also, binder coatings of various thickness may be employed, permitting precise control over the thickness of the coating on the paper. In essence the binder employed need serve only as an adhesive to hold the capsules to the paper. Only a small thin layer of binder is needed rather than a thick coating covering the capsules. Both aqueous binders and non-aqueous binders may be employed. Since non-aqueous binders may be used, it is not necessary to employ expensive papers thereby providing additional economies as well as a superior product. One of the particular advantages of the free-flowing powders of the invention is that it may be employed with a hot melt wax binder or dispersed in a printing ink vehicle. In the case of printing ink vehicles, the microscopic capsules may be dispersed in them and the resulting product may be printed on a paper sheet at the same time as ordinary ink printing is done.

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This is particularly satisfactory since it provides an excellent means of spot application whereby prescribed areas on the backs or fronts of the sheets of paper may be coated with capsules. This is one of the particular advantages of the present invention since it permits application of a transfer film or coating of capsules to only those areas of the paper where it is desired.

In order that the present invention may be better understood, the following examples of products prepared according to the invention are given for purposes of illustration. Although the number of film-formers, marking fluids, coloring and color-forming materials and binders is so great, and the number of combinations of materials suitable for making the capsules and record materials containing the capsules over an area thereof is vast, those skilled in the art will be able to readily practice the invention from reading the examples which illustrate the preparation of the products of the invention. Portions of components are given in terms of parts by weight, unless otherwise specified.

Example 1

This example describes the preparation of microscopic capsules prepared by spray drying an emulsion of mineral oil in aqueous hydroxyethylcellulose.

About 30 parts of 100 second mineral oil containing 4.5 parts of Mogul A (Godfrey Cabot, Inc.) carbon black (high volatile content--low oil absorption--336 Angstrom units mean diameter) was emulsified into 700 parts of a 10% aqueous

solution of hydroxyethylcellulose (having a viscosity of 250-350 Centipoises at 30° C. when in the form of a 5% aqueous solution). Emulsification was accomplished by agitating the 10% aqueous solution of hydroxyethylcellulose by itself in a Waring blender and then pouring in the oil solution slowly while agitation was continued. A fine particle size (one micron) stable emulsion was thus produced. The resulting emulsion was injected via a fine air feed nozzle into a heated spray drying chamber of a temperature of between about 225-265° F. and the dried product collected. On examination, microscopic capsules ranging from 1 to 10 microns were observed. The capsules exuded black oil when subjected to ordinary writing pressure.

Example II

This example describes the preparation of microcapsules by spray drying a hot emulsion of mineral oil in aqueous gelatin.

About 75 parts of 100 second mineral oil containing about 5% by weight of duPont Oil Blue A dye was emulsified into 725 parts of a hot 20% aqueous gelatin solution having a temperature of 60° C., prepared from high gel strength (300 gram strength) Viscomix gelatin employing the same emulsification procedure described in Example I. Upon spray drying the resulting emulsion in accordance with the process of Example I, a free-flowing powder was obtained of capsules having particle sizes from 1 to 70 microns in diameter.

Example III

This example describes the preparation of microscopic capsules prepared by spray drying an emulsion of mineral oil in aqueous hydroxyethylcellulose.

About 17 parts of 100 second mineral oil containing 5% by weight of the butyl ether of malachite green A was emulsified into 3000 parts of a 5% aqueous solution of Cellosize WP-40 (hydroxyethylcellulose which when in the form of a 2% aqueous solution at 20° C. possesses a viscosity of 75 to 125 centipoises). An emulsion was produced and then spray dried in accordance with the procedure of Example I. A free-flowing powder of microscopic capsules was obtained.

Example IV

This example describes the preparation of microscopic capsules containing a marking fluid containing a colorless color-forming dye intermediate.

About 4.5 parts of the butyl ether of methyl violet was dissolved in 100 parts of an equal part mixture of Arochlor 1254 (a chlorinated diphenyl having a Saybolt viscosity of 44-48 seconds at 210° F.), amyl diphenyl and amylnaphthalene. The resulting solution was colorless. This solution was emulsified into 600 parts of a 10% aqueous solution of hydroxyethylcellulose in accordance with the procedure of Example I and the resulting emulsion spray dried in accordance with Example I. A free-flowing powder of microscopic capsules having particle sizes from about 0.5 to 10 microns diameter was obtained.

When the capsules were subjected to pressure they exuded colorless marking fluid which produced a strong color when absorbed on a paper impregnated with a surface of attapulgite clay or a paper surface coated with tannic acid.

Example V

This example describes the preparation of microscopic capsules containing carbon black.

About 150 parts of a 10% Arochlor 1248 (a chlorinated diphenyl having a Saybolt viscosity of 36-37 seconds at 210° F.) and 90% 100 second mineral oil mixture containing 22.5 parts of carbon black was emulsified into 75 parts of an aqueous solution of water soluble urea-formaldehyde resin (Uformite 400-67% solids) and 2.5 parts of extra low viscosity (5-25 centipoises in a 2% aqueous solution at 25° C.) carboxymethylcellulose in 175 parts of water. The emulsion was produced in accordance with the procedure of Example I and diluted with 600 parts of water, and while continuing the rapid agitation, sufficient concentrated hydrochloric acid was added to produce condensation and precipitation of the urea formaldehyde resin. The resulting mixture was agitated for another five minutes, filtered, and the filter cake washed with water and acetone and then agitated with toluene to remove any free oily liquid. The mixture was again filtered and the filter cake air dried and then subjected to further drying at 105° C. Under microscopic examination the resulting dry, free-flowing powder was found to consist of agglomerated microscopic capsules ranging in diameter from between about

4 to 50 microns. On applying pressure to these capsules, the walls ruptured and black oil was exuded in copious quantities.

Example VI

This example describes the preparation of microscopic capsules prepared from an emulsion of mineral oil in cellulose acetate.

About 100 parts of 100 second mineral oil containing about 25% by weight of nigrosine dye was emulsified into a solution of 50 parts of cellulose acetate in 600 parts of acetone in accordance with the procedure of Example I. The resulting emulsion was sprayed through an aspirator into the air to evaporate the acetone and the resulting dry microscopic capsules collected. The capsules were of about 50 micron diameter particle size. When this free-flowing powder of capsules was subjected to writing pressure, the cellulose acetate shells of the capsules were ruptured and the oil containing the nigrosine exuded therefrom in copious quantities.

Example VII

About 171 parts of 100 second mineral oil containing about 15% by weight of duPont Oil Blue A was emulsified in accordance with the procedure of Example I into an aqueous solution of 57 parts of hydroxyethylcellulose (which in the form of a 5% aqueous solution at 20° C. had a viscosity of 50-150 centipoises) in 570 parts of water. The resulting emulsion was spray dried to provide a free-flowing powder of capsules having a diameter of between about 1 and 5 microns.

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The capsules exuded the blue colored fluid when subjected to pressure to give a blue mark on a receptive surface.

Example VIII

This example describes the preparation of capsules containing a colorless color-forming dye intermediate.

About 56 parts of 100 second mineral oil containing about 2 parts of the butyl ether of malachite green A (Color Index No. 657) in the alkaline condition was emulsified into a solution of 40 parts of gelatin and 1 part of sodium hydroxide in 200 parts of methanol. The emulsification was accomplished in accordance with the procedure of Example I. The resulting emulsion was spray dried by atomizing the emulsion into the air to provide micro-capsules ranging in size from about 1 to 60 microns. When the resulting capsules were coated to a sheet of paper and the sheet of paper placed in contact with the surface of an adjacent sheet which was coated with tannic acid, and pressure applied to the sheets in the form of pencil writing, a strongly colored mark was produced on the surface of the sheet containing the tannic acid.

Example IX

Microscopic capsules produced in accordance with Example III to the extent of 30 parts of free-flowing capsule powder was placed into 70 parts of a 5% solution of duPont isobutyl methacrylate in benzene. The resulting dispersion was applied to the backs of sheets of bond paper with a doctor blade and then subsequently air dried. The fronts of these sheets of paper had been sensitized with attapulgite clay. When a manifold of sheets were stacked one above the other, with the capsule coated surfaces adjacent to the clay

sensitized surfaces and writing pressure applied, a copy was produced on the fronts sensitized with clay at the sites where pressure was applied.

Example X

Microscopic capsules produced in accordance with Example VIII were placed in a flexographic vehicle (Bensing Bros. and Deeney D-536) (a water soluble protein dissolved in water) to the extent of 30 parts by weight of capsules and 70 parts of flexographic vehicle, to provide a printable ink which was applied to portions of a surface of sheets of paper by means of a Gravure roll which printed the desired portion of the surface of the sheets of paper with the capsule coating. The coating dried on the paper promptly. When the resulting coated sheets were assembled with the coated portions facing adjacent sheets activated with attapulgite clay and writing pressure applied against the treated surface, a strong colored mark was produced.

Example XI

About 30 parts of capsules produced in accordance with Example I were mixed with 70 parts of a mixture of 6 parts of cellulose acetate and 34 parts of acetone. The resulting mixture was applied to one surface of sheets of paper by means of a doctor blade. The sheets were permitted to dry in the air. The surface of the sheets of paper coated with the capsules provided an excellent means of copying.

Example XII

About 40 parts of paraffin wax having a melting point of 135°F. and 20 parts of FT-200 petroleum wax

(Fischer-Tropsch-1) were melted together at 120°C. Into the resulting molten mixture were added about 5 parts of Alpex resin (a cyclized rubber resin) and 120 parts of Schenectady ST-5115 resin and the resulting clear melt reheated to 120°C. and maintained at this temperature. About 125 parts of a solution of 5 parts of phenyl leuco auramine in 120 parts of butyl benzyl phthalate and 0.5 parts of dimethylethanolamine, heated to 120°C. was added with rapid agitation to the foregoing melt in a Waring blender. The emulsion so formed was sprayed via a hot air stream (150°C. temperature) inlet into a chilled atmosphere and the resulting spherical particles collected ranged in size from 1 to 60 microns. When subjected to writing pressures, these spheres ruptured and exuded the marking fluid which gave a strong blue coloration both on a paper sheet coated with Attapulgite clay and on a paper sheet coated with citric acid.

Example XIII

An emulsion was prepared by homogenizing 100 parts of a 50-50 mixture of polyethylene glycol 400 and ethoxy-triglycol containing 7 parts of Spirit Hectograph Black A (a black pigment)(General Dyestuff Co.) into a molten mixture of 50 parts of paraffin wax and 45 parts of Piccopale 100 (a petroleum hydrocarbon resin). The resulting emulsion was sprayed into a chilled atmosphere and the solidified particles containing the colored fluid collected and stored. The spheres possessed a particle size of from 1 to 60 microns.

Example XIV

About 50 parts of Geon 121 resin (polyvinyl chloride resin) was dispersed in 50 parts of dioctylphthalate as a plasticizer. Into this mixture was emulsified 50 parts of polyethylene glycol (mol. wt. 400) containing 5 parts of carbon black. The resulting emulsion was sprayed into an air chamber at a temperature of 350°F. in order to fuse the resin and plasticizer about the fluid colored particles to form capsules containing marking fluid.

Example XV

About 30 parts of capsules produced according to Example VIII were dispersed in 120 parts of a solution of 20 parts Alpex resin (a cyclized rubber resin) in 100 parts of Troluoil (a petroleum solvent prepared by straight-run overhead distillation) (Anderson-Prichard Oil Corp.) The resulting dispersion was reverse roll coated on to paper and the coating dried over rollers at 80°C. The coated paper gave a strong coloration when placed into contact with another paper coated with citric acid and both sheets subjected to ordinary writing pressures.

Example XVI

About 50 parts of capsules prepared according to Example I were dispersed in 50 parts of Geon 121 resin and 50 parts of dioctylphthalate to provide a paste. The resulting paste was printed on to paper and the coating cured by passing the coated paper over rollers at 350°F. An excellent copy sheet was produced.

As will be apparent from the foregoing examples various components of film-formers, plasticizers, marking fluids, dyes, pigments and binders may be employed. Listed below in Table 2 are some of the components which may be employed.

Table 2

Film Forming Resin or Polymer	Plasticizer	Resin Solvent or Dispersion Medium	Fluid For Dye or Pigment	Dye or Pigment	Binder	Binder Solvent or Dispersion Medium
Cellulose acetate	dibutyl-phthalate	acetone	mineral oil	oil soluble blue A (duPont).	carboxymethyl-cellulose.	water.
Hydroxyethyl-cellulose	polyethylene glycol 400.	water	rapeseed oil	carbon black	nitro-cellulose	methanol.
Zein	none	water methanol alkali.	mineral oil	butyl ether of crystal violet.	casein	water.
Gelatin	glycerol	water	methyl phthalyl-ethyl glycolate	methyl violet	hot-melt wax	none
Styrene-butadiene copolymer	none	water	chlorinated biphenyl.	malachite green lactone.	polyvinyl-chloride plastisol.	none.
Melamine-formaldehyde	none	water	amyl biphenyl	phthalo-cyanine blue pigment.	methyl-methacrylate.	toluene.
Polyvinyl-chloride	dioctyl adipate	none	poly-ethylene glycol 400.	crystal violet carbinol.	nitro-cellulose	methanol toluene.

Table 2 (cont'd.)

Film Forming Resin or Polymer	Plasticizer	Resin Solvent or Dispersion Medium	Fluid For Dye or Pigment	Dye or Pigment	Binder	Binder Solvent or Dispersion Medium
Polyvinyl acetate	none	water	cottonseed oil	ultra-marine blue	litho varnish	none
Polyvinyl-pyrrolidone	none	water	amyl-naphthalene	"Hectograph White A" duPont.	hot melt resin	none
Petroleum resin "Piccopale" (Penna. Indus. Chemical Co.)	paraffin wax mineral oil	none	thio-diethylene glycol	methyl violet	starch	water
Cyclized rubber	mineral oil	"Troluoil" (Anderson-Prichard Oil Corp.)	polyethylene glycol 400	"Cadmium Red Litho-pone Dup" Glidden.	cellulose acetate	acetone
Polyterpene resin "Piccolyte" (Penna. Indus. Chemical Co.)	paraffin wax mineral oil	none	glycerol	pigment	gelatin	water

It will be appreciated that if more than one copy is wanted it is possible to coat the capsules of the invention on at least a portion of one side of sheets of paper and, if necessary, a reactive coating on the other side, so that by placing a pile of such sheets one upon the other and pressing upon them with a pencil or subjecting them to the blow of a typewriter key, a suitable number of copies can be obtained depending upon the amount of pressure applied and the thickness of the paper.

The terms and expressions which have been employed are used as terms of description and not of limitation, and it is not intended, in the use of such terms and expressions, to exclude any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed.

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WHAT IS CLAIMED IS:

1. A free-flowing powder comprising microscopic discrete capsules comprising a rupturable shell containing therein a marking fluid capable of being liberated when the shells of said discrete capsules are ruptured upon being subjected to external pressure.

2. A substantially dry free-flowing powder comprising microscopic discrete capsules comprising a rupturable shell containing therein a marking fluid capable of being liberated when the shells of said discrete capsules are ruptured upon being subjected to external pressure, said capsules having a particle size of from between about 0.1 and 70 microns diameter.

3. A substantially dry free-flowing powder comprising microscopic discrete capsules comprising a rupturable shell containing therein a colored fluid capable of being liberated when the shells of said discrete capsules are ruptured upon being subjected to external pressure.

4. A substantially free-flowing powder as defined by Claim 3 wherein the colored fluid contains carbon black.

5. A substantially dry free-flowing powder comprising microscopic discrete capsules comprising a rupturable shell containing therein a marking fluid capable of being liberated when the shells of said discrete capsules are ruptured upon being subjected to external pressure, said marking fluid comprising a colorless material forming a color when brought into contact with another substance.

6. A substantially dry free-flowing powder as defined by Claim 5 wherein the colorless material is a colorless dye-former capable of producing a color when in the presence of an acidic substance.

7. A substantially dry free-flowing powder as defined by Claim 2 wherein the capsules have a particle size of between about 1 and 20 microns diameter.

8. A substantially dry free-flowing powder as defined by Claim 2 wherein the capsules have a particle size of between about 1 and 5 microns diameter.

9. A substantially dry free-flowing powder as defined by Claim 2 wherein the shell thickness of the capsules constitutes about one-tenth to one-third of the capsule diameter.

B 1066

10. A process of producing a free-flowing powder comprising microscopic discrete capsules comprising a rupturable shell containing therein a marking fluid capable of being liberated when the shells of said discrete capsules are ruptured upon being subjected to external pressure, which process comprises producing a dispersion of the marking fluid in a film-former in which the latter forms the discontinuous phase and is substantially insoluble in the marking fluid, and then drying said dispersion to produce said microscopic discrete capsules in the form of a free-flowing powder.

11. A process defined by Claim 10, wherein the drying is accomplished by spray drying.

12. A process defined by Claim 10, wherein the ~~dispersion is produced with a hot-melten film-former and the drying accomplished by chilling the dispersion.~~

13. A process as defined by Claim 10, wherein the resulting capsules which are produced have a diameter of between about 0.1 and 70 microns.

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23 ~~14~~. A record copying sheet having on at least a portion of one side thereof a coating of a free-flowing powder of microscopic discrete capsules comprising a rupturable shell containing therein a marking fluid capable of being liberated when the shells of said discrete capsules are ruptured upon being subjected to an external printing or marking pressure. C9

24 ~~15~~. A record copying sheet having on at least a portion of one side thereof a coating of microscopic discrete capsules comprising a rupturable shell containing therein a marking fluid capable of being liberated when the shells of said discrete capsules are ruptured upon being subjected to external pressure, said capsules being held to said sheet by a binder which is of a different substance from that forming the rupturable shell of said capsules. C9

25 ~~16~~. Paper having coated on at least a portion of a surface thereof microscopic discrete capsules comprising a rupturable shell containing therein a marking fluid capable of being liberated when the shells of said discrete capsules are ruptured upon being subjected to external pressure, said capsules being held to said sheet by a binder which is of a different substance from that forming the rupturable shell of said capsules. C9

26 ~~27~~. Paper as defined by Claim ~~1~~ 25 wherein the marking fluid comprises a colored transfer substance.

27 ~~18~~. Paper as defined by Claim ~~1~~ 25 wherein the marking fluid comprises a colorless material forming a color when brought into contact with another substance.

28 ~~19~~. Paper as defined by Claim ~~1~~ 25 wherein the marking fluid comprises a colorless dye-former capable of producing a color when in the presence of an acidic substance.

29 ~~20~~. Paper as defined by Claim ~~1~~ 25 wherein the capsules have a diameter of between about 0.1 and 70 microns..

21. The novel products and processes, as described in the foregoing specification, including the various features of novelty therein set forth, taken either singly and/or in combination.

Claim 5 "

" C1

" C3

" C4

" C5

" C6

" C7

" C8

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Oath, Power of Attorney, and Petition

Being duly sworn, I, NORMAN MACAULAY

depose and say that I am a citizen of Great Britain, residing at Niagara Falls, Niagara County, New York; that I have read the foregoing specification and claims and I verily believe I am the original, first, and sole inventor of the invention or discovery in

NOVEL MARKING PRODUCTS AND PROCESS

described and claimed therein; that I do not know and do not believe that this invention was ever known or used before my invention or discovery thereof, or patented or described in any printed publication in any country before my invention or discovery thereof, or more than one year prior to this application, or in public use or on sale in the United States for more than one year prior to this application; that this invention or discovery has not been patented in any country foreign to the United States on an application filed by me or my legal representatives or assigns more than twelve months before this application; and that no application for patent on this invention or discovery has been filed by me or my representatives or assigns, or with my knowledge or consent, in any country foreign to the United States.

And I hereby appoint LOUIS F. REED, Esq., 20 Exchange Pl., New York 5, N. Y., Registration No. 10,075, my attorney or agent with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith.

Wherefore I pray that Letters Patent be granted to me for the invention or discovery described and claimed in the foregoing specification and claims, and I hereby subscribe my name to the foregoing specification and claims, oath, power of attorney, and this petition, this

2nd day of August, 1937:

Inventor Norman — Macaulay.
First name — Middle Initial — Last Name

Post Office Address } 1837 Cleveland Avenue,
Niagara Falls, New York.

State of NEW YORK }
County of NIAGARA } ss.:

Before me personally appeared NORMAN MACAULAY, to me known to be the person described in the above application for patent, who signed the foregoing instrument in my presence, and made oath before me to the allegations set forth therein as being under oath, on the day and year aforesaid.

Charlotte A. Hammond
Notary Public

My commission expires [illegible]

SEAL

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ORIGINALLY FILED #2

FIG. 1

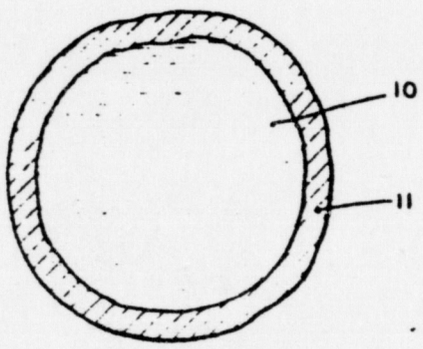

FIG. 2

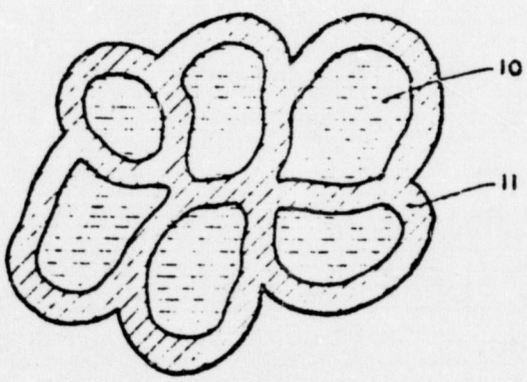

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FIG. 3

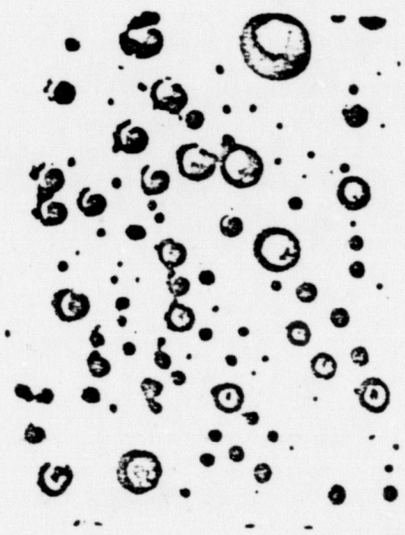
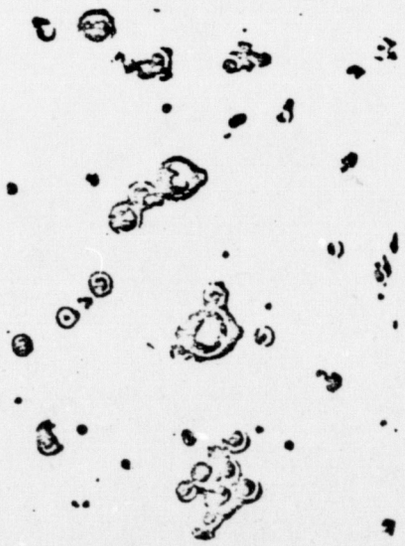


FIG. 4



below in Table 2 are some of the components which may be employed.

AUG 27 1957

U. S. PATENT OFFICE
SEP 9 1957
DIV. 25

IN THE UNITED STATES PATENT OFFICE

Division: 25
Applicants: Macaulay, Norman of Niagara Falls, N.Y.
Serial No.: 670,574
Filed: August 6, 1957.
For: Novel Marking Products and Process

NOTICE OF CHANGE OF ADDRESS

I, NORMAN MACAULAY, the applicant in this application, have changed my residence address to the following:

547 - 22nd Street, Niagara Falls, New York.

Respectfully submitted,

Norman Macaulay
Norman Macaulay

Dated, August 22, 1957.

POL-90
Rev.

ADDRESS ONLY
THE COMMISSIONER OF PATENTS
WASHINGTON 25, D. C.

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications respecting this application should give the serial number, date of filing and name of the applicant.

PAPER No. 4

Louis F. Reed
20 Exchange Place
New York 5, New York

Applicant: Norman Macaulay	
Ser. No. 676,974	MAILED
Filed August 9, 1957	DEC 12 1957
For NOVEL MARKING PRODUCTS AND PROCESS	

16—63457-6 GPO

Please find below a communication from the EXAMINER in charge of this application.

Robert C. Watson
Commissioner of Patents.

This application has been examined.

References applied:

Sandberg	2,711,375	June 21, 1955	117-36
Green (1)	2,712,507	July 5, 1955	117-36
Green (2)	2,800,457	July 23, 1957	117-36xr
Green (3)	2,800,458	July 23, 1957	117-36xr

Suitable legends should be applied to the drawings to render them self-descriptive.

Claims 1 to 13 are rejected as unpatentable over either Green (2) or Green (3). The Green references relate to methods of producing free-flowing powders of the type claimed. Note Green (3), col. 2, lines 43 to 52 wherein it is taught that the dry granules may be formed in free-flowing form by spray drying them. Also note Green (2), col. 1, lines 45 to 50 wherein it is taught that cooling is employed to form the gelled layer around the capsule. Various coloring materials, including dye and dye-forming materials, may be used.

Claims 14 to 20 are rejected as unpatentable over Green (2) or (3). These references teach that the granules discussed above may be applied to a paper base in the manufacture of a recording sheet. Several of the claims call for the use of a binder to hold the granules

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to the sheet, which binder is a different substance than that which is used to form the rupturable shell of the capsule. The Green patents teach that the granules are normally somewhat tacky and may be applied to paper without the use of binder. Furthermore, in view of the fact that these references disclose that the granules may be obtained in dry granular form it is considered to be merely a matter of choice and an unpatentable variation to disperse the granules in any desired binder material. Only obvious and expected results are obtained.

Claim 21 is rejected as being obviously non-statutory.

Summary:

Claims rejected: 1 to 21

Claims allowed: none

Examiner

MKatz/lml

JUN 1958

IN THE UNITED STATES PATENT OFFICE

Applicant: Norman Macaulay
Serial No.: 676,574
Filed: August 6, 1957
For: NOVEL MARKING PRODUCTS AND PROCESS

Division 25

New York 5, New York

June 9, 1958

Hon. Commissioner of Patents

Washington 25, D. C.

U. S. PATENT OFFICE
JUN 13 1958
DIV. 25

Sir:

AMENDMENT

In response to the Office Action of December 12, 1957, please amend the above identified application as follows:

Amend the drawings pursuant to the draftsman's letter which is submitted herewith.

Rewrite Claim 1 as:

--22. A free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer shell of film-forming material, said encapsulating outer shell being formed directly by evaporation forces on the solvent of a film-former solution which comprises the continuous phase of suspended minute particles of an emulsion, the discontinuous phase of which emulsion comprises the liquid droplets.--

Rewrite Claim 2 as:

--23. A free-flowing powder of microscopic discrete rupturable capsules comprising marking fluid droplets encapsulated within an outer shell of film-forming material, said encapsulating outer shell being formed directly by evaporation forces

Claim 23 (cont'd.)

on the solvent of a film-former solution which comprises the continuous phase of suspended minute particles of an emulsion, the discontinuous phase of which emulsion comprises the marking fluid droplets, said capsules being capable of being ruptured under pressure to release the encapsulated marking fluid.

Rewrite Claim 3 as:

--24. A free-flowing powder of microscopic discrete capsules as defined by Claim 23, wherein the marking fluid droplets are colored and the capsules have a particle size of from between about 0.1 to 70 microns diameter.--

Claim 4, line 2, cancel "3" and replace with --24--.

Rewrite Claim 5 as:

--25. A free-flowing powder of microscopic discrete capsules as defined by Claim 23, wherein said marking fluid comprises a colorless material forming a color when brought into contact with another substance.--

Claim 6, line 2, cancel "5" and replace with --25--.

Claim 7, line 2,
Claim 8, line 2, and
Claim 9, line 2, cancel "2" and replace with --22--.

Add the following claims:

--26. A free-flowing powder of microscopic discrete capsules as defined by Claim 22, wherein the encapsulating outer shell is formed by a condensation reaction.

--27. A free-flowing powder of microscopic discrete capsules as defined by Claim 22, wherein the encapsulating outer shell is formed by solidification resulting from heating.

--28. A free-flowing powder of microscopic discrete capsules comprising liquid droplets encapsulated within an outer shell of film-forming material, said encapsulating outer shell being formed by suspending minute particles of an emulsion in a gaseous atmosphere and cooling the hot molten film-former which comprises the continuous phase of said emulsion, the discontinuous phase of which emulsion comprises the liquid droplets.

--29. A free-flowing powder of microscopic discrete capsules as defined in Claim 28, wherein the liquid droplets comprise a marking fluid, said capsules being capable of being ruptured under pressure to release the encapsulated marking fluid.--

Rewrite Claim 10 as:

--30. A process for producing a free-flowing powder of microscopic ~~discrete~~ rupturable capsules comprising liquid droplets encapsulated within a rupturable outer shell of film-forming material, said encapsulating outer shell being formed directly by a non-ionizable water-soluble film-former evaporation forces on the solvent of a film-former solution, which comprises the continuous phase of suspended minute particles of an emulsion, the discontinuous phase of which

Claim 30 (cont'd.)
and between about 23% and 80% by weight of the capsules
emulsion comprises the liquid droplets, which process comprises producing an emulsion of the liquid droplets in a film-former solution in which the latter forms the continuous phase and is substantially insoluble in the liquid droplets, suspending minute particles of said emulsion in a gaseous atmosphere, and then subjecting said suspended emulsion particles to evaporation forces to produce said microscopic discrete capsules in the form of a free-flowing powder.~~4~~ 60c

(Add the following claims:)

~~4--31.~~ A process for producing a free-flowing powder of microscopic rupturable discrete capsules comprising marking fluid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell being formed directly by evaporation forces on the solvent of a film-former solution of a non-ionizable water-insoluble film-former which comprises the continuous phase of suspended minute particles of an emulsion, the discontinuous phase of which emulsion comprises the marking fluid droplets, which process comprises producing an emulsion and between about 23% and 80% by weight of the capsules
~~of the~~ marking fluid, suspending minute droplets ~~in a film-former in which the latter forms the discontinuous phase and is substantially insoluble in the marking fluid,~~ and then subjecting said suspended minute emulsion particles to evaporation forces to produce said microscopic discrete capsules in the form of a free-flowing powder.

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--32. A process as defined by Claim ~~31~~ wherein said marking fluid comprises a colored material.

Claim 11, line 1,
Claim 12, line 1, and
Claim 13, line 1, cancel "10" and replace with --30--.

Claim 11, line 2, cancel "drying" and replace with --evaporation--.

Claim 12, cancel the last two lines and replace with --emulsion is produced with a hot molten film-former as the continuous phase, and the formation of the film-forming encapsulating shell is accomplished by suspending minute particles of said emulsion in a gaseous atmosphere, and cooling the suspended particles.--

Add the following claims:

--33. A process as defined by Claim ~~12~~, wherein the resulting capsules have a diameter between about 0.1 and 70 microns.

--34. A process as defined by Claim 30, wherein the encapsulating outer shell is formed by a condensation reaction.

--35. A process as defined by Claim 30, wherein the encapsulating outer shell is formed by solidification resulting from heating.--

Claims 14 and 15, cancel the period at the end of each of the claims and add: --, said microscopic discrete capsules being those defined by Claim 23.--

Claim 16, cancel the period at the end of the claim and add: --, said microscopic discrete capsules being those defined by Claim 29.--

Cancel Claim 21.

REMARKS

Reconsideration of the application as amended is respectfully requested.

The drawings have been amended pursuant to the accompanying draftsman's letter to insert self-describing legends.

The claims have been substantially revised to more clearly distinguish over the prior art and expedite the allowance of the case. The revised claims will be discussed in greater detail hereinbelow.

Claim 21 has been cancelled.

Green Patents (2) and (3) relate to a tedious involved process for producing microscopic capsules involving an ill-defined phenomenon which Green refers to as "coacervation". In addition to employing the "coacervation" treatment, the patentee also combines this with gelling. Green's process involves a multitude of separate treatments and is limited to a restricted group of shell forming substances, namely, the gellable hydrophilic colloids. These materials are represented by gelatin, the alginates, gum Arabic,

Irish moss, etc. The complex process required by Green is exemplified by Fig. 6 of the drawings of Green patent 2,800,457, to which the applicant will refer. As shown in the flow sheet of Fig. 6, Green must first produce an emulsion of an oil in the gellable hydrophilic colloid material. After producing the emulsion and forming a sol, Green must carry out the following steps:

(1) Adjust the pH to 5 by adding sodium hydroxide;

(2) Mix the resulting emulsion or sol with about 500 to 550 grams of water;

(3) Again adjust the pH, this time to 4.4;

(4) Agitate the mixture and add a 37% solution of formaldehyde;

(5) During these foregoing treatments all of the ingredients must be maintained under rigid temperature control at 50° C;

(6) Further agitation is necessary, accompanied by rapidly reducing the temperature to 10° C. to produce a gel;

(7) The pH must again be adjusted, this time to 9, with sodium hydroxide; and

(8), (9) and (10) The aqueous dispersion containing formed microscopic capsules is then subjected to a hardening treatment, and if Green is to obtain a dry free-flowing product, he must employ the additional steps of drying the product and comminuting it.

In all Green has employed 10 steps requiring delicately controlled conditions to produce free-flowing microcapsules. In the accompanying photocopy of Fig. 6 of the drawing of the Green patent these steps have been numbered in accordance with the foregoing discussion.

The applicant's process, on the other hand, is manifestly simple requiring the initial formation of an emulsion of a film-former solution representing the continuous phase and a discontinuous phase which comprises liquid droplets. The applicant is then enabled to almost immediately produce his free-flowing microcapsules in only one additional operation, namely, simultaneous suspension of minute particles of an emulsion in a gaseous atmosphere and evaporation of the solvent of the film-former continuous phase solution or by merely cooling in the case where the film-former is a hot, molten material. Obviously, the applicant's process is greatly different from that of Green, and so is the product.

The applicant's process employs the initial preparation of an emulsion of a continuous phase comprising a film-former solution containing a solvent or a molten, hot material which solidifies on cooling and the discontinuous phase of which emulsion comprises minute liquid droplets, the droplets being converted to the free-flowing powder of microscopic discrete capsules by suspending minute particles of the emulsion in a gaseous atmosphere and directly evaporating the solvent from the film-former solution, or, in the case of the molten hot chillable material, cooling it so as to

provide a solid shell. The applicant's employment of a spray drier constitutes merely one suitable method of atomization and solvent evaporation. It is during this simultaneous atomization and solvent evaporation from the continuous phase of the emulsion that the applicant actually forms his dry, free-flowing microscopic discrete capsules. In the Green process, the microcapsules are formed by the combined "coacervation" and gellation treatment to form an aqueous dispersion of formed microcapsules. When Green spray dries his dispersion he is only drying a product which already contains previously formed existing microscopic capsules. Thus, Green's spray drying constitutes merely removal of the water from the dispersion. Thus, in substance, the applicant employs evaporation forces, for example, in a spray drier, to form the encapsulating shell and dry powder of his microscopic capsules. Green does not use a spray drier or evaporation to form a shell, since his shell and the capsules have already been formed in the aqueous dispersion.

The applicant's process and the resulting product are unique in that they employ evaporation forces to remove solvent from the continuous phase of an emulsion of suspended liquid droplets. As pointed out hereinabove, the applicant's process permits him to do in one step what Green requires ten steps to accomplish. This results quite obviously in economy and permits him to produce his microscopic capsules in the form of a free-flowing powder almost instantaneously, whereas Green requires a long series of delicate manipulations requiring a substantial amount of time and expense to produce dry discrete capsules.

Summarizing some of the salient distinctions of the applicant's product and process, applicant does not employ any "coacervation" or gelling treatments. The applicant's microscopic discrete capsules are not formed by using some intermediate dispersion but are instantly formed in the nature of a free-flowing dry powder.

The claims in the case have been substantially revised and a number of the claims replaced with new claims which are designed to more clearly distinguish the applicant's invention over the product and process of the Green patents.

New Claim 22 defines applicant's free-flowing powder of microscopic discrete capsules as comprising liquid droplets encapsulated within an outer shell of a film-former material. The claim next defines the particularly unique feature of the applicant's invention which constitutes forming the shell directly by evaporation forces on the solvent of a film-former solution which comprises the continuous phase of suspended minute particles of an emulsion, the discontinuous phase of which emulsion comprises the liquid droplets. This claim clearly distinguishes over the Green patents which teach a product in which spray drying is employed only to dry the aqueous phase of a dispersion which contains previously existing capsules. This claim is directed broadly to microcapsules which are not limited to containing a marking fluid. It is obvious to those skilled in the art that applicant's capsule product and process are suitable for producing capsule materials other than marking materials.

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Claim 23 is more limited than Claim 22 in that the liquid droplets are defined as marking fluid droplets and the capsules are capable of being ruptured under pressure to release the marking fluid.

Claim 24 is dependent upon Claim 23 and specifies that the marking fluid droplets are colored and the capsules have a particle size of between about 0.1 and 70 microns diameter.

Claim [illegible] is now dependent upon Claim 24.

Claim [illegible] is dependent upon and more limited than Claim 23 in specifying that the marking fluid comprises a colorless material forming a color when brought into contact with another substance.

Claim [illegible] is now dependent upon Claim 25 and Claims [illegible] and [illegible] are now dependent upon Claim 22.

Claim [illegible] is a new claim dependent upon Claim 22, specifying that the outer shell is formed by a condensation reaction. This claim is supported by [illegible] of the specification.

Claim [illegible] is a new claim dependent upon Claim 22, specifying that the encapsulating outer shell is formed by solid plastics resulting from melting. This claim is supported by [illegible] of the specification which is directed to the preparation of a capsule employing plastisol technique.

Claim [illegible] defines a free-flowing powder of microencapsulated [illegible] wherein the encapsulating outer shell is formed by cooling a hot [illegible] mixture. This claim is the product counterpart of [illegible].

Claim [illegible] is dependent upon Claim [illegible] and specifies that the liquid [illegible] comprises a [illegible] fluid.

Claim [illegible] is dependent upon Claim [illegible] over

the Green patents since they are directed to a product which is clearly not taught by the prior art.

Claim 30 is a process claim which is the process counterpart of product claim 22 and which is directed to the applicant's novel process of producing an emulsion of liquid droplets in a film-former solution in which the latter forms the discontinuous phase of the emulsion and is substantially insoluble in the liquid droplets and by suspending minute particles of the emulsion in a gaseous atmosphere, and by evaporation forces producing the free-flowing powder of microscopic discrete capsules.

Claim 31 is more limited than Claim 30 in specifying that the liquid droplets are marking fluid droplets.

Claim 34 is dependent upon Claim 31 and is more limited in specifying that the marking fluid comprises a colored material.

Claims 11, 12 and 13 have been made dependent upon Claim 30.

Claim 11 has further been amended to specify that the evaporation is achieved by use of a spray drier (not merely drying a dispersion of previously formed capsules as in the Green patents).

Claim 12 has been amended to specify that the film-former encapsulating shell is formed by suspending minute droplets of the emulsion in a gaseous atmosphere, and by chilling the hot molten film-former continuous phase. This is the process counterpart of product claims 21 and 29 and is distinguished over the Green patents. The cooling of the Green patent to which the examiner has referred relates to gellation of the "coacervate." The "coacervate" of Green is

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formed around the oil droplets before cooling and cooling merely gels the "coacervate." On the other hand, the applicant forms a capsule shell by solidification (cooling) of the molten hot phase of suspended emulsion droplets by exposure to an atmosphere which is at a temperature below the melting point of the film-former. No gel formation is involved in the applicant's process. As pointed out in connection with Fig. 6 of Green patent 2,800,457, a photocopy of which is attached, the applicant is able to convert his emulsion to a dry powder of free-flowing capsules in one cooling operation. This is by virtue of employing molten film-former material. Consequently, it is submitted that Claim 12 is manifestly patentable over Green.

Claim 33 is dependent upon Claim 12 and specifies that the capsules have a diameter of between about 0.1 and 70 microns.

Claim 34 is dependent upon Claim 30 and is the process counterpart of product claim 26.

Claim 35 is dependent upon Claim 30 and is the process counterpart of product Claim 27.

Claims 14 and 15, directed to the applicant's novel record copying material, have been amended to define the capsules as those of product Claim 23. Similarly, Claim 16 defines the capsules as those of Claim 29. Applicant's record copy sheets possess significant advantages over the products of the Green patents. The Green patents disclose the preparation of capsules which are produced in aqueous dispersions and it is the aqueous dispersions which Green contemplates applying to paper. This technique possesses a number of disadvantages, including the tendency of the

water to corrugate the paper and cause it to buckle and warp, even when using special expensive paper. On the other hand, the applicant's product can be applied in a number of binders which are not aqueous (and therefore do not buckle or warp or corrugate the paper).

In view of the foregoing, it is considered necessary to have an aqueous coating, such as Green, coated by the paper mill during manufacture of the paper because it is not feasible to do so in the printing plant where a wide variety of papers are immediately available and can be coated on the basis of individual customers orders. Such advantageous printing plant coatings, combined with the tremendous and extremely costly inventories required when the paper mill must do the coating, gives the applicant's non-aqueous coatings (for printing plant use) very outstanding advantages over Green. Furthermore, the paper mill is unable to make spot coatings in restricted areas on the paper, and since Green's aqueous coating is not suitable for printing plant use and applicant's non-aqueous coatings are suitable, an additional advantage of the applicant becomes very apparent.

In his remarks the Examiner has stated that the Green patents teach that their granules are normally somewhat tacky and may be applied to paper without the use of a binder. This is one of the reasons why the applicant's product is significantly superior to the Green patents. The applicant is able to produce in one step (as against 10 steps of Green) a product which is not tacky but is in the form of a free-flowing dry powder. This product requires a binder when applied to paper and in so using a binder a more uniform, more durable and more smudge-proof product is obtained. Furthermore, as mentioned hereinabove, the coating

may be applied to paper at the printing plant.

It is, therefore, submitted that applicant's claims, as amended, clearly distinguish over the cited art. The Examiner has referred to, but not applied to the claims, the Sandberg patent and Green patent No. 2,712,507, for reasons which are apparent. These references are not as pertinent as the two Green patents which the Examiner has relied upon.

Since the application is believed to be in condition for allowance, prompt allowance is respectfully requested.

Respectfully submitted,

Louis J. Reed

Attorney for Applicant

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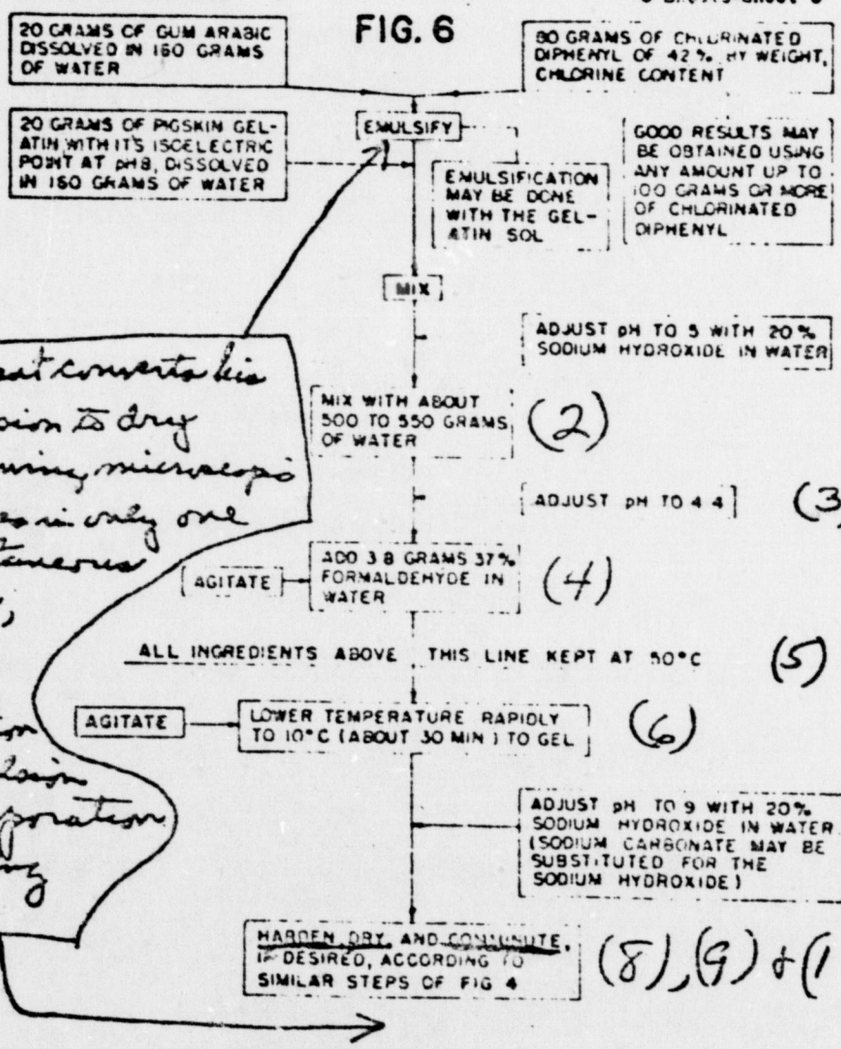
July 23, 1957 B. K. GREEN ET AL 2,800,457

OIL-CONTAINING MICROSCOPIC CAPSULES AND METHOD OF MAKING THEM

Filed June 30, 1953 3 Sheets-Sheet 3

FIG. 6



applicant converts his emulsion to dry free-flowing microscopic capsules in only one simultaneous operation, namely, combining atomization of the emulsion with evaporation or cooling

INVENTORS
BARRETT K GREEN
LOWELL SCHLEICHER

BY Earl Beard
Jr. & Sons
THEIR ATTORNEYS

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Form PO-140
Form approved by Comptroller General, U. S.
November 2, 1950

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE

DEPOSIT ACCOUNT ORDER FORM

BEFORE USING THIS ORDER FORM read the important information on the reverse side

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Date: June 9, 1958

Account No.: 06-1075

Order No.:

Name of Depositor: FISH, RICHARDSON & NEAVE

Street Address: 20 EXCHANGE PLACE

City, Zone, State: NEW YORK 5, N. Y.

Total amount of charge, $ CORRECTED

MAR 1 5 1963

DESCRIPTION OF ARTICLES OR SERVICES TO BE FURNISHED

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Div: 25
Applicant Norman Macaulay
Ser. No. 673,578
Filed: August 6, 1957
For: Novel Marking Products and Process

Please apply the following legends to the four figures of the drawings:

Under Fig. 1 insert: "MAGNIFIED CROSS-SECTION OF DISCRETE CAPSULE ACCORDING TO THE INVENTION"

Under Fig. 2 insert: "MAGNIFIED CROSS-SECTION OF A CLUSTER OF DISCRETE CAPSULES ACCORDING TO THE INVENTION"

Under each of Figs. 3 and 4 insert: "PHOTOMICROGRAPH MAGNIFIED 1,000 TIMES OF DISCRETE CAPSULES ACCORDING TO THE INVENTION"

If additional space is needed attach separate sheet.

(Signature)

THIS FORM MAY BE REPRODUCED WITHOUT PERMISSION OF THE PATENT OFFICE.

16—64460-8

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U. S. PATENT OFFICE

JUN 1 [illegible]6

DIV. 25

Letter to Dft'sm.

IN THE UNITED STATES PATENT OFFICE

Division: 25
Applicant: Norman Macaulay
Serial No.: 676,574
Filed: August 6, 1957
For: Novel Marking Products and Process

New York 5, New York

June 9, 1958

Hon. Commissioner of Patents

Washington 25, D.C.

DRAFTSMAN'S LETTER

Sir:

The Patent Office Draftsman is hereby authorized to apply the following legends to the four figures of drawings, pursuant to the first paragraph of the Office Action of December 12, 1957, in this application.

Under Fig. 1 insert: "MAGNIFIED CROSS-SECTION OF DISCRETE CAPSULE ACCORDING TO THE INVENTION".

Under Fig. 2 insert: "MAGNIFIED CROSS-SECTION OF A CLUSTER OF DISCRETE CAPSULES ACCORDING TO THE INVENTION"

Under each of Figs. 3 and 4 insert: "PHOTOMICROGRAPH MAGNIFIED 1,000 TIMES OF DISCRETE CAPSULES ACCORDING TO THE INVENTION".

It is requested that the charges for this work be charged to the account of Fish, Richardson & Neave, New York 5, New York. A deposit account order form is enclosed for this purpose.

Respectfully submitted,

Louis J. Rood

Attorney for Applicant

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B,1065

IN THE UNITED STATES PATENT OFFICE

Applicant: Norman Macaulay
Serial No.: 576,574
Filed: August 6, 1957
For: NOVEL MARKING PRODUCTS AND PROCESS

Division 25

New York 5, New York

September 2, 1958

U. S. PATENT OFFICE
SEP 5 1958
DIV. 25

Hon. Commissioner of Patents

Washington 25, D. C.

Sir:

SUPPLEMENTAL AMENDMENT

Please correct the Amendment filed June 11, 1958 as follows:

Claim 31, cancel lines 10 through 12 inclusive and replace with the following--of the marking fluid in a film former solution in which the latter forms the continuous phase and is substantially insoluble in the marking fluid, suspending minute particles of said emulsion in a gaseous atmosphere,--

Page 11, line 7, cancel "discontinuous" and replace with --continuous--.

REMARKS

The purpose of the Amendment is to correct two errors in the Amendment filed June 11, 1958 which have been called to the attention of the applicant's attorney. As amended, Claim 31 is now in accordance with applicant's process and page 11, line 7, now correctly identifies the phase of the film-former solution.

Respectfully submitted,

Louis J. Reed

Attorney for Applicant

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THE COMMISSIONER OF PATENTS
WASHINGTON 25, D. C.

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications respecting this application should give the serial number, date of filing, and name of the applicant.

PAPER No. 8

Louis F. Reed
20 Exchange Place
New York 5, N.Y.

Applicant: Norman Macaulay	
Ser. No. 676,574	MAILED
Filed August 6, 1957	DEC 1 6 1958
For NOVEL MARKING PRODUCTS AND PROCESS	PAT OFF

16—63457-4 GPO

Please find below a communication from the EXAMINER in charge of this application.

Robert C. Watson
Commissioner of Patents.

Responsive to amendments filed June 11 and September 3, 1958.

Additional references:

Wallenmeyer	2,650,895	Sept. 1, 1953	167-81
Hochberg	2,777,798	Jan. 15, 1957	167-81

Claims 4, 6-9 and 22-29 are rejected as unpatentable over Green (2). This reference relates to free-flowing powders of the type claimed. The process limitations are not proper in the article claims and may not be relied on to patentably distinguish over the article of the reference. Furthermore, it is pointed out that the particular process of manufacture will not be evident in the final product. Note page 10, lines 24 to end of page of the specification wherein it is taught that the emulsion may be spray dried or the continuous film forming material first condensed around the emulsified droplets by curing or other means and then spray dried. Also, see Example V, page 23. This condensation treatment is similar to that taught by the Green reference.

Claims 14-20 are rejected as unpatentable over Green (2). This reference teaches that the granules

containing the marking fluid may be applied to a paper substrate. It is considered that the use of a particular binder on a non-aqueous carrier, is an obvious and unpatentable expedient whenever it is desired to avoid moistening the paper, when such paper is deleteriously affected by such wetting.

Claims 11-13 and 30-35 are rejected as unpatentable over Green (2) in view of Wallenmeyer, newly cited. The Green reference relates to a process of manufacturing free-flowing powder of the type described. The powder is formed while in emulsion form and the spray dried to remove carrier fluid. It is considered to be merely a matter of choice and an unpatentable variation to form the finely divided particles in any well known manner, such as by a spraying process. Such a spray process is disclosed by the Wallenmeyer reference, note the statement in col. 5, lines 29-34 of this reference.

Claims 4, 6-9 and 22-29 are rejected as failing to properly define the stated invention. The product should be defined in terms of its structure and not by the method of manufacture.

Hochberg is made of record. This reference discloses the manufacture of liquid containing globules which are made by spraying a hot composition into a cool atmosphere.

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Summary:

Claims cancelled: 1-3, 5, 10 and 21.

Claims rejected: 4, 6-9, 11-20 and 22-35.

Claims allowed: None.

M.KATZ:les

Examiner

MAIL ROOM JUN 5 1959 U.S. PATENT OFFICE

B 1071Y

IN THE UNITED STATES PATENT OFFICE

Applicant: Norman Macaulay
Serial No.: 670,374
Filed: August 6, 1957
For: NOVEL MARKING PRODUCTS AND PROCESS

Division 25

New York 5, N.Y.

June 4, 1959

Hon. Commissioner of Patents

Washington 25, D.C.

U. S. PATENT OFFICE JUN 9 1959 DIV. 25

Sir:

AMENDMENT

In response to the Office Action of December 1[illegible], 1958, please amend the above-identified application as follows:

Add the following claim:

--[illegible]. A free-flowing powder of microscopic discrete rupturable capsules having a particle size of between about 0.1 and 70 microns diameter, said capsules comprising liquid droplets encapsulated within an outer shell rupturable under pressure, said liquid droplets being substantially insoluble in and incapable of dissolving said outer shell and comprising between about 23% and 80% by weight of said capsules, said outer shell having a thickness comprising from about one-tenth to one-third of the capsule diameter and comprising a material selected from the class consisting of a non-ionizable water-soluble film-former and a hydrophobic water-insoluble film-former.--

suitable for producing capsule materials other than water-soluble materials.

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Cancel Claims 4, 6, 9, 24 and 25, without prejudice.

Claims 22 and 23, line 2 of each claim, insert before "capsules" the word --rupturable--;

line 3 of each claim, after "shell" insert --rupturable under pressure--;

cancel the period at the end of each claim and add --, said liquid droplets comprising between about 23% and 80% by weight of the capsules, and said encapsulating outer shell being formed from a non-ionizable water-soluble film-forming material.--

Claims 7 and 8, line 2 of each claim, cancel "22 and replace with --36--.

Rewrite Claim 26 as:

--37. A free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer shell rupturable under pressure, said liquid droplets comprising between about 23% and 80% by weight of the capsules, said encapsulating outer shell being formed of a hydrophobic water-insoluble film-forming material produced by a condensation chemical reaction.--

Rewrite Claim 27 as:

--38. A free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer shell rupturable under pressure,

said liquid droplets comprising between about 23% and 80% by weight of the capsules, said encapsulating outer shell being formed from a hydrophobic water-insoluble film-forming material by solidification from heating.--

Rewrite Claim 28 as:

--39. A free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer shell rupturable under pressure, said liquid droplets comprising between about 23% and 80% by weight of the capsules, said encapsulating outer shell being formed from a hydrophobic water-insoluble film-forming material by cooling hot molten non-aqueous film-forming material.--

Cancel Claim 29, without prejudice.

Rewrite Claim 12 as:

--40. A process for producing a free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell being formed from a hot molten non-aqueous film-former comprising the continuous phase of an emulsion, the discontinuous phase of which emulsion comprises liquid droplets comprising between about 23% and 80% by weight of the emulsion, which process comprises producing an emulsion of the liquid droplets in said hot molten non-aqueous film-former in which the latter forms the continuous phase and is substantially insoluble in the liquid droplets, suspending minute particles of said emulsion in a gaseous atmosphere, and cooling the suspended particles to solidify said film-former and produce microscopic discrete rupturable capsules in the form of a free-flowing powder.--

patent to which the examiner has referred relates to gella-
tion of the "coacervate." The "coacervate" of Green is

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Claims 30 and 31, lines 2 of each claim, after "discrete" insert --rupturable--

lines 3 of each claim, after "outer" insert --rupturable--

Claim 30, line 5, after "solution" insert --of a non-ionizable water-soluble film-former--

Claim 30, line 8, after "droplets" insert --and between about 23% and 80% by weight of the capsules--

Claim 31, line 6, after "solution" insert --of a non-ionizable water-soluble film-former--

Claim 31, line 9, after "droplets" insert --and between about 23% and 80% by weight of the capsules--

Claim 33, line 1, cancel "12" and replace with --40--

Rewrite Claim 34 as:

--41. A process for producing a free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell consisting of a hydrophobic water-insoluble material produced by the chemical condensation of the reactive constituents of the film-former dissolved in aqueous solution, said solution comprising the continuous phase of an emulsion, the discontinuous phase of which emulsion comprises liquid droplets comprising between about 23% and 80% by weight of the capsules, which process comprises producing an emulsion of the liquid droplets in said aqueous solution of film-former constituents, causing said film-former constituents to undergo chemical condensation about the liquid droplets, and thereby produce said microscopic discrete rupturable capsules in the form of a free-flowing powder.--

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contemplates applying to paper. This technique possesses a number of disadvantages, including the tendency of the

B 1070

Rewrite Claim 35 as:

9--42. A process for producing a free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell being formed of a plastisol film-former comprising the continuous phase of an emulsion, the discontinuous phase of which emulsion comprises liquid droplets comprising between about 23% and 80% by weight of the capsules, which process comprises producing an emulsion of the liquid droplets in said plastisol film-former in which the latter forms the continuous phase and is substantially insoluble in the liquid droplets, heating minute particles of said emulsion to thereby produce said microscopic discrete rupturable capsules in the form of a free-flowing powder.

Claims 14, 15 and 16, cancel the previous amendment added to the last line of each claim and replace with 41, said microscopic discrete capsules being those defined by claim 11.

REMARKS

Reconsideration of the application as amended is respectfully requested.

The most recent Office Action has been carefully considered and the claims have been substantially revised in the light of the Examiner's comments to more adequately distinguish applicant's invention over the references and to more clearly set forth the applicant's contribution. Also, a number of the claims have been cancelled solely to reduce the number of pending claims and issues in the case and thereby simplify examination.

uniform, more durable and more smudge-proof product is obtained. Furthermore, as mentioned hereinabove, the coating

Claims 4, 6-9 and 22-29 have been rejected by the Examiner on the ground that they are unpatentable over the Green (2) patent and on the ground that they fail to properly define the invention. Claims 4, 6, 9, 24 and 25 have been cancelled, without prejudice, solely to restrict the number of claims pending in the case. New Claim 36 has been added in the light of the Examiner's suggestion that applicant's microscopic rupturable capsules should be defined in terms of their structure and not the method of manufacture. While the applicant disagrees with the Examiner's suggestion that product claims are improper if the product is defined in terms of its process of preparation, Claim 36 has been introduced as a claim of the type that the Examiner has indicated would be more suitable. Upon favorable action on newly added Claim 36, applicant will give careful consideration to revising the other product claims along the same lines.

The Examiner's rejection of the capsule claims as being unpatentable over the Green (2) patent has been carefully considered. These claims have been either amended or rewritten and are now submitted to clearly distinguish the applicant's invention over the Green (2) patent. As was pointed out in a previous amendment, the Green patent is concerned with a vaguely-defined phenomenon which the patent refers to as "coacervation." The process described involves a large number of separate treatments employing as the shell-forming or film-forming substances mixtures of certain ionizable, gellable, water-soluble hydrophilic colloids, namely mixtures of gelatin and gum Arabic. These substances are markedly different from those contemplated in the applicant's

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product. The applicant's film-forming substances are set forth generally on page 13 of the applicant's specification. These film-formers fall primarily into two general classifications, the non-ionizable water-soluble film-formers and the hydrophic water-insoluble film-formers. Among the first group are hydroxyethyl cellulose (see examples 1, 3, 4 and 7) and methyl cellulose. While these materials are water-soluble they are not salt-forming and are therefore substantially unionized when dissolved in aqueous solution. These materials are clearly different from those of the Green patent which must be ionizable as well as water-soluble in order to undergo the so-called "coacervation" treatment. Applicant's non-ionizable water-soluble film-formers and hydrophobic water-insoluble film-formers on the other hand, being non-ionizable, do not undergo the coacervation phenomenon.

The applicant's second group of film-formers, namely, the hydrophobic water-insoluble film-formers, are the many resinous or polymeric materials and waxes, both natural and synthetic, set forth on page 13 of the specification and in the working examples (note examples 5, 6, 12, 13 and 14). These film-forming materials are vastly superior to the film-formers of the Green patent by virtue of the substantial water-insolubility of the shell or film which then forms. Because the shells or films are insoluble in water, the capsules are less subject to attack by atmospheric moisture. Also, such capsules will permit encapsulation of water-miscible fluids, such as the glycols, which could not be employed in the Green capsules. Yet, they are readily fractured or ruptured when compressed or subjected to pressure, thereby releasing the fluid contents of the capsule. It is therefore submitted that applicant's capsules differ substantially from the capsules of the Green patent in their composition and are there-

As has been pointed out previously, the Green patent requires a multi-stage process in which an emulsion must first be produced after which 10 separate steps must be carried out before a capsule is obtained. By virtue of the materials which the applicant employs as the film-former, namely, the non-ionizable water-soluble film-formers and the hydrophobic water-insoluble film-formers, applicant is enabled to produce his capsules by means of a simple 1-or 2-stage process which omits the many separate stages necessary in the process of the Green patent. It is submitted that this then provides a substantial improvement over the product of the Green patent and results in a product richly deserving of patent protection.

Turning now to the capsule claims, new Claim 36 defines applicant's microscopic discrete rupturable capsules, having a particle size of between about 0.1 and 70 microns diameter, in which the capsules form a free-flowing powder with the capsules comprising liquid droplets encapsulated with a rupturable outer shell. The claim has been limited to specify that the shell and the liquid droplets are insoluble in each other, with the liquid droplets comprising between about 2% and 80% by weight of the capsules. It is this ratio which enables the applicant to provide a shiny rupturable capsule. The basis for these proportions is found on page 11 of the specification at lines 4 through 8. The claim further specifies that the outer shell shall have a thickness of from about 1/10 to 1/2 of the capsule diameter. The thickness was the basis of original claim 5, now cancelled. The claim next specifies the applicant's all-important film-forming materials. These features of the claim clearly distinguish over the Green patent and the

Claims 22 and 23 have each been amended to specify that the capsules and the outer shell are rupturable under pressure. These claims also now specify that the liquid droplets shall comprise between about 23% and 80% by weight of the capsules. Since these claims define a capsule produced by a suspension-evaporation process, which process is amenable to use with a non-ionizable water-soluble film-forming material, the claims now specify this type of outer shell. It is submitted that these claims are clearly patentable over the prior art.

Claims 7 and 8 have been made dependent upon new Claim 36.

Claim 26 has now been rewritten as new Claim 37. This claim defines applicant's capsules having a shell of a hydrophobic water-insoluble film-forming material produced by a condensation chemical reaction. These capsules are of the type produced by Example V of the specification. The claim further specifies that the liquid droplets comprise between about 23% and 80% by weight of the capsule.

Claim 27 has been rewritten as new Claim 38, which is similar to new Claim 37, except that it refers to the product produced by encapsulating by means of solidification of a plastisol or organosol in accordance with Example XIV of the specification.

Claim 28 has been rewritten as new Claim 39 and is also similar to new Claim 37, except that it defines the product produced by cooling hot molten non-aqueous film-forming material. This claim is exemplified by Examples XII and XIII of the specification.

Claim 29 has been cancelled, without prejudice, to reduce the number of claims pending in the case.

It is submitted that the revised claims directed to the capsule are now clearly patentable over the Green patent or any of the prior art. The Green patent product is produced by employing an ionizable water-soluble gellable hydrophilic colloid by an intricate process called "coacervation." Applicant, on the other hand, employs different materials which are in no way suggested by the prior art, and process of preparation which is clearly different from that of Green. The claims, as revised, now clearly define applicant's invention in terms of its distinguishing characteristics.

It is noted that the Examiner has suggested that Example V on page 23 of applicant's specification is a condensation similar to that taught by the Green patent. This is certainly not the case. Nowhere does the Green patent disclose any condensation chemical reactions of the type of Example V. Applicant's Example V employs a polymerization reaction by which a hydrophobic water-insoluble cross-linked urea-formaldehyde resin is formed. This is markedly different from anything suggested by the "coacervation" of Green.

Reconsideration is respectfully requested of the rejection of Claims 14-20 as being unpatentable over Green (2). These claims have now been amended to refer back to new capsule Claim 36, which defines the capsules in terms of structure as suggested by the Examiner. The applicant recognizes that he is not the first to apply a marking capsule to a copying sheet, but he is the first one to provide a copying sheet having his unique microscopic discrete rupturable capsules affixed to it. The resulting copy sheets possess significant advantages over the sheets of the Green patent. The Green patent requires the preparation of

capsules in the form of aqueous dispersions and it is this aqueous dispersion which the patentee applies to the paper. This technique possesses many disadvantages, including the tendency of water to corrugate the paper and cause it to buckle and warp, even though specially prepared expensive paper is employed. The applicant's capsules on the other hand, are obtained as a free-flowing dry powder and can be applied in a number of binders which are not aqueous and, therefore, do not buckle, warp, or corrugate the paper. This is much more than an obvious expedient as suggested by the Examiner. The use of a non-aqueous binder is just not feasible with the teachings of the Green patent, yet in the case of applicant's invention it is not only feasible, but preferred. In view of the results achieved by the applicant's copying sheet and the difference in the character of the capsules employed, it is submitted that these claims are clearly patentable over the prior art.

Process claims 11-13 and 30-35 have been rejected as unpatentable over Green (2) in view of the Wallenmeyer patent. The Examiner has incorrectly alleged that the Green patent teaches a process of the applicant's type. The Green patent is concerned with the process involving "coacervation" along with gellation treatment whereby he forms an aqueous dispersion of substantially completely formed capsules. When Green spray-dries this aqueous dispersion, he is drying and removing only the dispersing water. Thus in Green's spray-drying, only the water of dispersion is removed. On the other hand, when the applicant employs evaporation forces as provided by a spray-drier, he is forming both the encapsulating shell and the dry powder of his microscopic capsules at the same time. This rapid process permits the

Claims 14-20 are rejected as unpatentable over Green (2). This reference teaches that the granules

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steps as compared with the 10 or more steps required by the Green patent. It is submitted that any process which reduces the steps necessary from 10 to 1 or 2 must constitute a patentable contribution.

As has been pointed out hereinabove in connection with the capsule claims, applicant employs a film-forming substance which is quite different from that of the Green patent. The Green patent employs ionizable water-soluble hydrophilic colloidal materials only. Applicant, on the other hand, employs non-ionizable water-soluble materials or hydrophobic water-insoluble materials. This is a major distinction, which when considered with the differences in the process steps thoroughly distinguishes applicant's processes from the process of the Green patent.

The Wallenmeyer patent adds nothing to the shortcomings of the Green patent. This patent admittedly spray-dries a vitamin emulsion but nothing is said about the size of the particles produced. Also, what is even more important, the Wallenmeyer patent is not concerned with the production of rupturable products of any sort such as is essential to the applicant's processes and invention. The Wallenmeyer patent discloses at most the use of an emulsion containing only 8% by weight of liquid which could finally become encapsulated. With such a small proportion of liquid in the capsule, the Wallenmeyer product is not readily rupturable, as is the case with applicant's processes employing about 23% to 80% liquid. Nor is rupturability one of the things which Wallenmeyer would desire. He is concerned with protecting vitamins A and D from oxidative decomposition and the thicker the coating employed, the less contact will the

vitamins have with oxygen from the atmosphere and the less decomposition. Consequently, Wallenmeyer was trying to achieve something quite different from the goal of the applicant. The applicant is concerned with the production of capsules which will rupture readily to exude their liquid contents. He has found that to achieve this the liquid content of the capsules should be between about 23 and 80% by weight of the capsules.

Furthermore, the Wallenmeyer patent employs as the coating material sugars and dextrins which are quite different from the film-formers which the applicant desires to employ and particularly different from the hydrophobic water-insoluble film-formers. It is therefore submitted that the applicant's processes are manifestly patentable over the references.

Turning now to the process claims, Claim 12 has been rewritten as new Claim 40. This claim is directed to the applicant's process for producing free-flowing rupturable capsules by means of cooling small particles of an emulsion of a hot molten non-aqueous film-former to solidify the film-former and thereby provide a free-flowing powder of capsules. This claim is directed to the process of Examples XII and XIII of the application. The claim further specifies that the droplets shall comprise between about 23 and 80% by weight of the capsule-forming emulsion. This process is altogether different from anything suggested by the references. There is no drying at all involved in this process since, by definition, the film-former does not contain substantially any water. An emulsion of a liquid discon-

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tinuous phase and a continuous phase of a hot molten wax-type film-former is employed with the wax solidifying upon cooling to form the shell of microscopic rupturable capsules. This process is completely foreign to anything suggested by the references and is therefore submitted to be manifestly patentable.

Claims 30 and 31 are directed to applicant's suspension-evaporation process. These claims have been amended to emphasize that a rupturable capsule and shell are produced and that the droplets shall comprise between about 23 and 80% by weight of the capsules. As stated above, this provides a readily rupturable capsule. The claims have been further modified to specify that a non-ionizable water-soluble film-former is employed in the process. These features now clearly distinguish the claims from the references.

Claim 33 has now been made dependent upon Claim 40.

Claim 34 has now been rewritten as new Claim 41. This claim is directed to the process of producing the capsules employing a film-former which becomes hydrophobic and water-insoluble as a result of undergoing chemical condensation. This type of process is illustrated particularly by Example V of the present specification, whereby a water-insoluble hydrophobic cross-linked urea formaldehyde polymer is formed to provide the capsule shell. The claim specifies that the liquid droplets comprise between about 23 and 80% by weight of the capsules. This process is not even remotely suggested by the references and the claim is, therefore, submitted to be clearly patentable.

Claim 35 has been rewritten as new Claim 42. This claim is directed to applicant's process whereby the film-former is a plastisol or organosol as employed in Example XIV of the specification. In accordance with this process the emulsion, in which the continuous phase is a plastisol, is finely divided and heated to form a rigid plastisol coating and thereby to produce capsules in the form of a free-flowing powder. The claim specifies that the liquid droplets shall comprise between about 23 and 80% by weight of the capsules. This process is also thoroughly remote from the references and therefore submitted to be manifestly patentable.

It is noted that the Examiner has given no consideration to the patentability of the processes which are the subject of Claims 40, 41 and 42. Possibly he has overlooked the significance of these processes. Since the prior art fails to suggest them, they are submitted to be clearly patentable.

The Examiner has made of record a Hochberg patent, but has not applied it to the claims. The patent has been considered, but is considered to be of no pertinence to the present invention. Apparently the Examiner also considered this patent lacking in relevance, since he did not apply it to the claims. This patent is concerned with producing small particles, but there any resemblance to the present invention ends. The Hochberg patent clearly sets forth that it is concerned with the production of pellets which are entirely <u>solid throughout</u> and of substantially homogeneous composition throughout. The Examiner's attention is respectfully invited to column 5,

sulated within an outer shell rupturable under pressure,

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lines 13-22, column 8, lines 55 through 71 and column 9, lines 17-22 of the patent wherein the patentee states repeatedly that the mass is substantially uniform throughout and upon solidifying becomes solid throughout. Such capsules are not rupturable and are not useful for the purposes of the present invention. Consequently it is submitted that this patent is not pertinent to the present invention.

It is, therefore, submitted that the applicant's claims, as amended, clearly distinguish over the prior art. The application is now believed to be in condition for allowance and such action is respectfully requested.

Respectfully submitted,

Louis F. Reed

Attorney for Applicant

minute particles of said emulsion in a gaseous atmosphere, and cooling the suspended particles to solidify said film-former and produce microscopic discrete rupturable capsules in the form of a free-flowing powder.

3. 67

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U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications respecting this application should give the serial number, date of filing, and name of the applicant.

PAPER No. 10

Louis F. Reed
20 Exchange Pl.
New York 5, N. Y.

Applicant:	Norman Macaulay
Ser. No.	676,574
Filed	Aug. 6, 1957
For	NOVEL MARKING PRODUCTS AND PROCESS

MAR 3 1960
PAT DIV 25

Please find below a communication from the EXAMINER in charge of this application.

Robert C. Watson
Commissioner of Patents.

Responsive to amendment filed June 5, 1959.

Claims 7, 8, 22, 23 and 36-39 are rejected as unpatentable over Green (2). As pointed out before this reference relates to free-flowing powder of the type claimed and differs only in the manner of forming the powder. The process of manufacture will not be evident in the final product. Further, such limitations may not properly be set forth in the article claims since they are not necessary to describe the article. Applicant argues that the film-forming material of Green is ionizable and water-soluble whereas the claimed material is non-ionizable and water-soluble. It is not clear that this difference exists. Note that many types of materials are set forth on page 13 of the specification. The film-former is described as either water-soluble or organic solvent-soluble. Included are animal glues (line 6) which certainly includes gelatin, the material described by Green. Further, in view of the many materials disclosed, and their wide range of properties, it appears clear that applicant considers all film-formers to be suitable. The choice of any particular film-former will depend only on the type of coating desired and the nature of

a free-flowing powder.--

4. 68

the material to be encapsulated. All of these materials have certain well-known advantages and disadvantages, such as relative price, nature of solvent necessary, effect on the substrate, etc. and it is merely a matter of choice to employ a suitable film-former for a given use. Further, it has not been shown or even alleged that the ionizing property of the film-former has any effect at all on value of a particular substance as a film-former in the formation of capsules. The capsules of Green have the same physical dimensions of those claimed.

Claims 14-20 are rejected as unpatentable over Green (2), which reference discloses that capsules containing marking fluid may be applied to paper. It is obvious that the carrier fluid for the capsules may be varied depending on the binder employed for the capsules and the nature of the substrate.

Claims 11, 13, 30-33 and 40-42 are rejected as unpatentable over Green (2) in view of Wallenmeyer. The Wallenmeyer is cited to show that it is well known to encapsulate oily fluids by first emulsifying said fluids in a film-forming material and then spraying fine droplets thereof into a drying atmosphere. It is considered to be merely a matter of choice and an unpatentable expedient to employ such technique to form the capsules of Green. Obviously the size of the dispersed phase and the droplets sprayed will be varied in accordance with the type of droplet it is desired to form. Several of the claims relate to the continuous phase being in hot melt form and the globules being formed by spraying into a cool atmosphere. This is also well known in the art and is shown, for example, by Hochberg, of record. Note, furthr that Hochberg discusses waxy film-formers. It is considered that the formation of capsules of the size and nature claimed is

to more clearly set forth the applicant's contribution. Also, a number of the claims have been cancelled solely to reduce the number of pending claims and issues in the case and thereby simplify examination.

known, as taught by Green. The use of any particular well known method of forming fine capsules and the nature of the film-forming material appears to be merely matters of choice and yield only the expected properties in the article.

Claims 22, 23 and 37-39 are rejected as failing to properly define the stated invention. The product should be defined in terms of its structure and not by the method of manufacture.

Claims 7, 8, 11, 13-20, 22, 23, 30-32 and 36 are rejected as being drawn to new matter. There is no basis in the original specification for the limitation "non-ionizable water-soluble film former". It is clear from a reading of the specification that this property has not been recognized or taken advantage of in any way. Further, it is not apparent that the animal glue materials disclosed on page 13 do not have this property.

Summary:

Claims cancelled: 1-6, 9, 10, 12, 21, 24-29, 34 and 35

Claims rejected : 7, 8, 11, 13-20, 22, 23, 30-33 and 36-40

Claims allowed : none.

As an issue has been reached this rejection is made FINAL.

M.KATZ:mh

Examiner

markedly different from that contemplated in the applica-

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11

APPEAL NO. 331-60

IN THE UNITED STATES PATENT OFFICE

Applicant: Norman Macaulay
Serial No.: 6[illegible],774
Filed: August 6, 1957
For: NOVEL MARKING PRODUCTS AND PROCESS

Division 25

MAIL ROOM SEP 8 1960 PATENT OFFICE

New York 5, N.Y.
September 1, 1960

Hon. Commissioner of Patents
Washington 25, D.C.

Sir:

NOTICE OF APPEAL

Applicant hereby appeals to the Board of Appeals from the Examiner's action of March 3, 1960, in finally rejecting the pending claims. It is submitted that the Examiner erred in rejecting the claims for the various grounds cited.

A check for $25.00 is enclosed to cover the appeal fee.

Respectfully submitted,

Louis J. Reed
Attorney for Applicant

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compressed or subjected to pressure, thereby releasing the fluid contents of the capsule. It is therefore submitted that applicant's capsules differ substantially from the capsules of the Green patent in their composition and are therefore patentable over Green.

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#12

B'd

IN THE UNITED STATES PATENT OFFICE

BEFORE THE BOARD OF APPEALS

Applicant:	Norman Macaulay	Division 25
Serial No.:	670,574	
Filed:	August 6, 1957	APPEAL NO.
For:	NOVEL MARKING PRODUCTS AND PROCESS	39,169

BRIEF ON BEHALF OF NORMAN MACAULAY

This is an appeal from the decision of the Primary Examiner of Division 25 in finally rejecting Claims 7, 8, 11, 13-20, 22, 23, 30-33 and 36-42, inclusive, of the above entitled application. A copy of the claims on appeal is appended hereto.

An oral hearing is requested.

THE INVENTION

The invention on appeal relates to an important and significant contribution in the field of encapsulation. More specifically, the invention relates to microscopic discrete rupturable capsules in the form of a dry free-flowing powder containing within a rupturable shell an encapsulated liquid, and to a novel process for the production of the capsules. The invention also relates to copying sheets having on at least a portion of one side thereof a coating of the microscopic discrete rupturable capsules of the invention containing within the rupturable shells of the capsules a marking fluid capable of being liberated when the shells are ruptured by subjecting them to external printing or marking pressures.

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diameter. The thickness was the basis of original claim 5, now cancelled. The claim next specifies the applicant's all-important film-forming materials. These features of the claim clearly distinguish over the Green patent and the other prior art.

Appellant's microscopic discrete rupturable capsules are extremely small, having a particle size of between about 0.1 and 70 microns diameter. Contained within the outer shell, which is rupturable under pressure, is a liquid droplet which is substantially insoluble in and incapable of dissolving the outer shell. The encapsulated liquid droplet comprises between about 23% and 80% by weight of the capsules, with the outer shell having a thickness which is about 1/10 to 1/3 of the capsule diameter. The encapsulated liquid may take many forms and it may be an adhesive, medicinal, dye, perfume, chemical reagent, etc., or, as emphasized in the present specification, a marking fluid. One of the great advantages of the capsules of the present invention is the great versatility in the variety of the liquids which may be encapsulated. Within the concept of appellant's invention liquids of many types, either hydrophilic or hydrophobic, may readily be encapsulated by highly efficient and inexpensive means, by selecting a suitable film-forming or shell-forming encapsulating materials from among those disclosed in the present specification. Thus by selecting a film-forming material in which the liquid to be encapsulated is insoluble and incapable of being dissolved by that liquid, it is possible to encapsulate liquids of a great number of types. This is a particular advantage, since the prior art in this field was limited either to a hydrophobic liquid or a hydrophilic liquid but not both types which placed a serious limitation upon the usefulness of the prior art methods.

XII and XIII of the specification.

Claim 29 has been cancelled, without prejudice, to reduce the number of claims pending in the case.

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Appellant's novel microscopic discrete rupturable capsules are particularly useful in the copying field. Thus one of the important uses of appellant's capsules, which is emphasized in the present specification, is in the preparation of copying materials of the type that the layman often refers to as "carbon paper". Thus by encapsulating minute droplets of a marking fluid and coating at least a portion of one side of a copying sheet, such as a sheet of paper, and subjecting the copying sheet to writing or printing pressures, the capsules on the sheet which are subjected to the pressure rupture, thereby liberating the marking fluid which transfers to an adjacent copy material, producing an image. The marking fluid may be of a number of types, such as an oily hydrophobic fluid containing suspended therein particles of carbon black or an oil soluble colored dye. Systems are also available and disclosed in the present specification in which a colored marking fluid is contained in a hydrophilic liquid. In accordance with another type of marking capsule, a liquid containing a colorless, color-forming dye intermediate may be encapsulated and the capsules applied to one side of a copying sheet. Such a copying sheet is used in combination with a copy-receiving sheet which has on its receiving surface a chemical capable of reacting with the colorless color-forming dye intermediate encapsulated on the copying sheet to produce a colored image. When writing or typing pressure is applied

vide a copying sheet having his unique microscopic discrete rupturable capsules affixed to it. The resulting copy sheets possess significant advantages over the sheets of the Green patent. The Green patent requires the preparation of

to the copying sheet, it causes the capsules to rupture thereby liberating the fluid containing the colorless, color-forming dye intermediate which flows to the adjacent copy-receiving sheet containing the chemical co-reactant or developing agent on the receiving surface which causes the dye to undergo a chemical reaction and produce a color. This system is disclosed in greater detail in the present specification starting at page 17, line 4 through page 18, line 25 and in Examples III, IV, VIII, IX, X, XII and Table 2.

One of the particular advantages of the microscopic discrete rupturable capsules of the invention containing a marking fluid, whether colored or color-forming, is that when the capsules are applied to business forms for use in copying systems they do not tend to prematurely transfer or cause offset on the adjacent copy receiving sheets. In the preparation of business forms the copy materials must undergo a great deal of handling in their assembly, cutting, perforation, etc. Since the marking fluid is encapsulated in a discrete separate microscopic capsules, the passage of the sheets over mill rolls, punching of holes, perforating and guillotining of the edges of the paper tends to produce less undesirable smudging or offset because the liquid is retained in the capsule until it is eventually liberated by intentional writing and typing pressures applied to the paper.

the other hand, when the applicant employs evaporation forces as provided by a spray-drier, he is forming both the encapsulating shell and the dry powder of his microscopic capsules at the same time. This rapid process permits the applicant to provide his free-flowing powder in only 1 or 2

Another great advantage of the marking capsules of the invention is their great flexibility and versatility in the application of the capsules to the surface of paper. Appellant's capsules will permit application to papers using non-aqueous coating systems. Aqueous coating of capsules on paper requires more expensive paper and even with this type of paper there is frequently obtained unwanted buckling, distortion, and warping of the papers since water tends to strike through and warp the paper. Additionally, where an aqueous coating system is employed it is extremely difficult, if not impossible, to apply marking capsules to a limited area on one side of a sheet of paper. Aqueous systems usually require continuous coating over the entire sheet. Since many types of capsules in accordance with the present invention may be applied to paper using non-aqueous binders or coating materials, appellant's product does not suffer from the difficulties concomitant with aqueous coating. In particular, where a non-aqueous binder is employed, the free-flowing capsules of the invention may be applied to paper when dispersed in a printing ink vehicle. The coating of capsules may be applied to paper in much the same way as ordinary line printing is done. Thus prescribed areas on the backs or fronts of paper may be coated with capsules in accordance with the present invention.

It is therefore believed to be apparent that appellant's microscopic discrete rupturable capsules and copying sheets having them applied to it provide many desirable advantages.

tecting vitamins A and D from oxidative decomposition and the thicker the coating employed, the less contact will the

The appellant's process for producing his microscopic discrete rupturable capsules is a highly efficient, inexpensive, manifestly simple one requiring, at most, two steps. In the initial step, an emulsion is prepared in which a film-former solution constitutes the continuous phase surrounding a discontinuous phase comprised of liquid droplets, such as liquid droplets of a marking fluid. In only one additional operation appellant is enabled to produce his free-flowing powder of microscopic discrete rupturable capsules. In accordance with one type of emulsion system, employing a non-ionizable water-soluble film-former solution, this additional operation comprises suspending minute particles of the emulsion in a gaseous atmosphere and subjecting the suspended particles to evaporative forces. In accordance with another system of the present invention, employing a hot molten non-aqueous film-former, minute particles of the emulsion are subjected to a cooling action. In accordance with another type of emulsion, such as where the film-former phase contains constituents which undergo chemical condensation, the additional condensation step takes place in a liquid medium, with the formation of a rigid thermosetting polymer shell. In accordance with another type, employing an organosol or plastisol type of film-former, minute particles of the emulsion are subjected to heating action to form the capsule shells. The efficiency and advantages of this process over the prior art, particularly Green patent No. 2,800,457, employing at least 10 steps, will become apparent when the prior art is discussed.

It is submitted that appellant's process constitutes a particularly significant step forward.

THE REJECTION

The Primary Examiner has rejected capsule product and record copying sheet claims 7, 8, 14-20, 22, 23 and 36-39 as being unpatentable over Green et al patent No. 2,800,457. Process Claims 11, 13, 30-33 and 40-42 had been rejected as unpatentable over the same Green et al patent in view of Wallenmeyer patent No. 2,650,895. Claims 22, 23 and 37-39 have been rejected as failing to properly define the invention and Claims 7, 8, 11, 13-20, 22, 23, 30-32 and 36 have been rejected as being drawn to new matter. The references will be discussed first.

Green Patent No. 2,800,457

The Green patent relates to a tedious, time-consuming, involved process for producing microscopic capsules involving a vaguely-defined phenomenon which Green refers to as "coacervation". In addition to employing the "coacervation" phenomenon, the patentee combines this with gelling. The process of the Green patent involves a multitude of separate treatments employing as the shell-forming or film-forming substances, a mixture of certain ionizable, gellable, hydrophilic, water-soluble colloids, namely, mixtures of gelatin and gum Arabic. These shell-forming or film-forming substances are markedly different from those which are the subject of appellant's claims. The appellant's claims specify the use of film-formers or

shell-formers of two general classes. These are the (1) non-ionizable water-soluble class and the (2) hydrophobic water-insoluble class.

Among the first class of film-formers are hydroxyethyl cellulose (see examples I, III, IV and VII) and methyl cellulose. While these materials are water-soluble, they are not salt-forming and are therefore substantially unionized when dissolved in aqueous solution. These materials are clearly different from those of the Green patent which must be ionizable as well as water soluble. It is necessary that the Green patent materials be ionizable in order to undergo the "coacervation" phenomenon. It is submitted that this is obvious from the nature of the "coacervation" phenomenon described in the Green patent. Appellant's non-ionizable hydrophilic water-soluble film-formers and hydrophobic water-insoluble film-formers on the other hand, being non-ionizable, could not undergo the "coacervation" phenomenon.

The Examiner has questioned the distinction between ionizable and non-ionizable. While appellant's specification discloses some film-formers which are ionizable, the claims have been restricted to the non-ionizable type, which is exemplified by methyl cellulose and hydroxyethyl cellulose among the hydrophilic film-formers, in order to clearly distinguish over the prior art. It is submitted that the non-ionizable characteristics of these materials are well-known and require no further elaboration. Where the claims

are directed to a particular class of materials, it is not relevant that other classes of materials may be disclosed in the appellant's specification or will produce a capsule. The classes specified in appellant's claims are those which he has found to provide most satisfactory results.

Appellant's second class of film-formers, namely, the hydrophobic water-insoluble film-formers, are the many resinous or polymeric materials and waxes, both natural and synthetic, set forth on page 13 of the specification and in the working examples (note particularly examples V, VI, XII, XIII and XIV). These film-forming materials are vastly superior to the film-formers of the Green patent by virtue of the substantial water-insolubility of the shell or film which they provide. Since the shells or films are insoluble in water, the capsules are less subject to attack by atmospheric moisture and water. Also, such capsule shells will permit encapsulation of water-miscible fluids, such as the glycols, which could not be employed in producing the Green capsules, since they are soluble in the film-former. Yet, shells of appellant's hydrophobic water-insoluble film-formers provide capsules which contain a water-soluble liquid encapsulated therein. The ability to encapsulate hydrophilic or water-soluble liquids provides a great advantage of appellant's invention and it is submitted that those claims directed to the use of hydrophobic water-insoluble film-formers are particularly distinguished over and patentable over the Green patent.

It is, therefore, submitted that appellant's capsules differ substantially from the capsules of the Green patent in their composition and are patentable over Green.

An even more serious shortcoming of the Green patent is the process which it discloses. This process is a complex, involved, difficultly-controlled process requiring a large number of steps to produce a capsule. After producing an emulsion, the Green patent requires 10 separate steps before a free-flowing powder of capsules is obtained. By virtue of the materials which the appellant employs as the film-former, namely, the non-ionizable water-soluble film-formers and the hydrophobic water-insoluble film-formers, he is enabled to produce his capsules by means of a simple 1-or 2-stage process which omits the many separate stages necessary in the process of the Green patent. This then provides a substantial improvement over the product and process of the Green patent and results in a product and process richly deserving of patent protection.

The complex, involved, multi-stage process of the Green patent is exemplified by Fig. 9 of the drawings of the Green patent to which appellant will refer. As shown in the flow sheet of Fig. 6 Green must first produce an emulsion of an oil in the ionizable gellable hydrophilic colloid film-forming materials. After producing the emulsion and

forming a sol, Green must carry out the following steps:

(1) Adjust the pH to 5 by adding sodium hydroxide;

(2) Mix the resulting emulsion or sol with about 500 to 550 grams of water;

(3) Again adjust the pH, this time to 4.4;

(4) Agitate the mixture and add a 37% solution of formaldehyde;

(5) During these foregoing treatments all of the ingredients must be maintained under rigid temperature control at 50° C;

(6) Further agitation is necessary, accompanied by rapidly reducing the temperature to 10° C. to produce a gel;

(7) The pH must again be adjusted, this time to 9, with sodium hydroxide; and

(8), (9) and (10) The aqueous dispersion containing formed microscopic capsules is then subjected to a hardening treatment, and if Green is to obtain a dry free-flowing product, he must employ the additional steps of drying the product and comminuting it.

In all, Green has employed 10 steps requiring delicately controlled conditions to produce microscopic microcapsules. Attached hereto as Exhibit "A" is a reproduction of Fig. 6 of the drawing of the Green patent and these steps have been numbered in accordance with the foregoing discussion.

Appellant's process, on the other hand, is manifestly simple requiring the initial formation of an emulsion of a film-former solution representing the continuous phase and a discontinuous phase which comprises the liquid droplets. The appellant is then enabled to almost immediately produce his free-flowing microcapsules in only one additional operation such as by simultaneous suspension of minute particles of an emulsion in a gaseous atmosphere and evaporation of the solvent of the film-former continuous phase solution or by merely cooling in the case where the film-former is a hot, molten water-insoluble material, as in Examples XII and XIII and Claims 39 and 40. Where the film-former is a plastisol or organosol, as in Example XIV and Claims 38 and 42, the emulsion is first finely-divided and heated to form a rigid plastisol coating. Where the film-former is a material capable of undergoing chemical condensation such as will form a cross-linked urea-formaldehyde polymer as in Example V and Claims 37 and 41, droplets of emulsion are formed in an aqueous solution and polymerized until the shell is formed and hardens.

The Examiner has made much of the fact that the Green patent process uses a spray drier and in one of its types of capsule formation, appellant's process may use this device. The appellant's employment of a spray drier constitutes merely one suitable method of atomization and

solvent evaporation. It is during this simultaneous atomization and solvent evaporation from the continuous phase of the emulsion that the appellant actually forms his dry, free-flowing microscopic discrete capsules. In the Green process, the capsules are already formed and the shells hardened by the combined "coacervation" and gellation treatment to form an aqueous dispersion of formed capsules. When Green spray dries this dispersion he is only drying a product which already contains previously formed existing microscopic capsules. Thus, Green's spray drying constitutes merely removal of the water from the dispersion. Thus, in substance, the appellant employs evaporation forces, for example, in a spray drier, to form the encapsulating shell and dry powder of his microscopic capsules. Green does not use a spray drier or evaporation to form a shell, since his shell and the capsules have already been formed in the aqueous dispersion.

The appellant's process and the resulting product are unique in that they employ evaporation forces to remove solvent from the continuous phase of an emulsion of suspended liquid droplets. As pointed out hereinabove, the appellant's process permits him to do in one step what Green requires ten steps to accomplish. This results quite obviously in economy and permits him to produce his microscopic capsules in the form of a free-flowing powder almost instantaneously, whereas Green requires a long series of delicate manipulations requiring a substantial amount of time and expense to produce dry discrete capsules.

Obviously, appellant's process is greatly different from that of the Green patent, and so is the product.

Wallenmeyer Patent No. 2,650,895

The Wallenmeyer patent has been cited to try to bolster the rejection of the process claims in hopes of overcoming the shortcomings of the Green patent as a reference against the appellant's process. The Wallenmeyer patent overcomes none of the shortcomings of the Green patent as a reference. This patent admittedly spray-dries a vitamin emulsion but nothing is said about the size of the particles produced. Also, what is even more important, the Wallenmeyer patent is not concerned with the production of rupturable products of any sort such as is essential to the appellant's processes and invention. The Wallenmeyer patent discloses at most the use of an emulsion containing only 8% by weight of liquid which could finally become encapsulated. With such a small proportion of liquid in the capsule, the Wallenmeyer product is not readily rupturable, as is the case with appellant's processes employing about 23% to 80% liquid. Nor is rupturability one of the things which Wallenmeyer would desire. He is concerned with protecting vitamins A and D from oxidative decomposition and the thicker the coating employed, the less contact will the vitamins have with oxygen from the atmosphere and the less decomposition. Consequently, Wallenmeyer was trying to achieve something quite different from the goal of the appellant. Appellant

is concerned with the production of capsules which will rupture readily to exude their liquid contents. He has found that to achieve this the liquid content of the capsules should be between about 23 and 60% by weight of the capsules. This feature is set forth in appellant's claims and is quite different from the concept of Wallenmeyer.

Furthermore, the Wallenmeyer patent employs as the coating material sugars and dextrins which are quite different from the film-formers and shell-formers which the appellant desires to employ and particularly different from the hydrophobic water-insoluble film-formers of appellant. It is therefore submitted that the appellant's processes are manifestly patentable over any combination of the Green and Wallenmeyer patents.

Hochberg Patent No. 2,777,798

This Hochberg patent has been made of record by the Examiner and discussed in the rejection of the process claims, although the Examiner apparently does not base his rejection directly on this patent. The alleged relevance of the Hochberg patent is not understood. Apparently, the Examiner has serious doubts about its relevance since he has not based his rejection of the claims upon it. The Hochberg patent is concerned with producing small particles, but there any similarity to the present invention ends. The Hochberg patent

clearly sets forth that it is concerned with the production of pellets which are entirely solid throughout and of substantially homogeneous composition throughout. Column 5, lines 13-22, column 6, lines 55 through 71 and column 9, lines 17-22 of the patent state repeatedly that the mass is substantially homogeneous throughout and upon solidifying becomes solid throughout. The pellets could not be other than homogeneous throughout because the components are soluble in one another. Such pellets are not rupturable and are not useful for the purposes of the present invention. Consequently, it is submitted that this patent is not pertinent to the present invention.

The specific grounds of rejection of the Examiner will now be discussed.

The Rejection of Capsule Product Claims 7, 8, 22, 25 and 36-39 As Unpatentable Over the Green Patent

The shortcomings of the Green patent as a reference have been discussed hereinabove. While the Green patent may provide a free-flowing powder of capsules, he employs different film-formers and thereby obtains a shell which is different from that of appellant's capsules. Appellant's invention provides a greater flexibility in the choice of materials for producing satisfactory capsules and his capsules may be produced much more efficiently and easily than the production of capsules employing the complicated process of the Green patent.

The Examiner has challenged whether a difference exists between the ionizable film-formers of the Green patent and the non-ionizable film-forms of appellant's claims. The appellant has explained the differences in the discussion of the Green patent. Since appellant's capsules are different from those of the Green patent and provide advantages not provided by those of the Green patent, it is submitted that appellant's capsules are clearly patentable over the Green patent.

The Rejection of Record Copying Sheet Claims 14-20 As Unpatentable Over the Green Patent

Copying sheet Claims 14-20 define a record copying sheet having applied on at least a portion of one side thereof a coating of capsules in accordance with appellant's invention and as defined by Claim 36. While the Green patent discloses the application of capsules containing a marking fluid to paper, he does not disclose or suggest capsules in accordance with appellant's invention, since he was not aware of them. Copying sheets in accordance with appellant's invention, having applied thereto his capsules, provide significant advantages over the sheets of the Green patent. The Green patent requires the preparation of capsules in the form of aqueous dispersions and it is these aqueous dispersions which the patentee applies to the paper. This technique possesses many disadvantages, including the tendency of water to corrugate the paper and cause it to buckle and warp, even

though specially prepared expensive paper is employed. The appellant's capsules on the other hand, are obtained as a free-flowing dry powder and can be applied in a number of binders which are not aqueous and, therefore, do not buckle, warp, or corrugate the paper. This is not just an expedient. The use of a non-aqueous binder is just not feasible with the teachings of the Green patent, yet in the case of appellant's invention it is not only feasible, but preferred. In view of the results achieved by the appellant's copying sheet and the difference in the character of the capsules employed, it is submitted that these claims are clearly patentable over the prior art.

The Rejection of Claims 11, 13, 30-33 and 40-42 As Unpatentable Over the Green Patent in View of the Wallenmeyer Patent

The long, involved and complicated process of the Green patent and its shortcomings have been discussed in detail hereinabove. Appellant's process, on the other hand, requires not 10 separate steps but only one or two steps in order to produce the discrete microscopic rupturable capsules of the present invention. It is submitted that on this basis the Green patent can in no way be considered as suggesting or teaching appellant's process. The Wallenmeyer patent is concerned with something entirely different from discrete microscopic rupturable capsules and he, as well as Green, employs distinctly different shell-formers than those of the present invention. In view of the great disparity in the goals of the

Green and Wallenmeyer patents, it is submitted that they are not properly combinable. However, even when combined, it is submitted that they in no way suggest or teach appellant's novel process. The Examiner has alluded to the Hochberg patent as disclosing waxy film-formers. It is submitted that this patent is utterly lacking in any teaching of film-formers. Hochberg obviously cannot produce capsules, but only solid homogeneous pellets in which there is no film or shell formed. Consequently, the teachings of the Hochberg patent cannot be relevant.

The prior art particularly fails to teach or suggest appellant's process of employing a film-former which is a hot molten water-insoluble material in which the shell is formed by cooling the film-former as set forth in Claim 40. This is also true of appellant's system of employing a plastisol or organosol film-former in which the film-former is converted to a solid shell by heating the plastisol or organosol as set forth in Claim 42. Also particularly distinguished from the prior art is the process of Claim 41 wherein the film-former is a material capable of undergoing a condensation reaction in which droplets of the emulsion are dispersed in an aqueous solution and a polymer formed by the chemical condensation.

The Rejection of Claims 22, 23 and 37-39 As Failing to Properly Define the Invention

The Examiner has criticized these claims because they define the product in terms of process steps. It is submitted that while appellant has presented claims which are independent of the process, this should not defeat the patentability of product claims setting forth process steps. The claims objected to have been presented as alternate claims to product Claims 7, 8 and 36 which are independent of process limitations. Upon the allowance of claims of either type, appellant would cancel claims of the other type.

The Rejection of Claims 7, 8, 11, 13-20, 22, 23, 30-32 and 36 As Being Drawn to New Matter

The Examiner has contended that the expression "non-ionizable water-soluble film former" finds no basis in the original specification. Appellant recognizes that this precise language was not used in the original specification. However, appellant discloses film-formers having these characteristics, such as methyl cellulose and hydroxyethyl cellulose. Since these film-formers are known to have these properties, it is submitted that this disclosure supports the language to which the Examiner has objected.

In view of the foregoing, it is submitted that the Examiner's grounds of rejection are without foundation.

THE CLAIMS

In discussing the claims they will be grouped in three classifications, namely, (A) capsule product claims,

(B) record copying sheet claims and (C) process claims.

A. Capsule Product Claims

Capsule Claim 36 was introduced in accordance with the Examiner's suggestion that the capsules be defined in terms of their structure, regardless of their method of manufacture. This claim defines appellant's microscopic discrete rupturable capsules, having a particle size of between about 0.1 and 70 microns diameter, in which the capsules form a free-flowing powder with the capsules comprising liquid droplets encapsulated with a rupturable outer shell. The claim specifies that the shell and the liquid droplets are insoluble in each other, with the liquid droplets comprising between about 23% and 80% by weight of the capsules. It is this ratio which enables the appellant to provide a suitably rupturable capsule. The claim further specifies that the outer shell shall have a thickness of from about 1/10 to 1/3 of the capsule diameter. The claim next specifies the appellant's all-important film-forming materials, namely, non-ionizable water-soluble or hydrophobic water-insoluble film formers. These features of the claim clearly distinguish over the Green patent and the other prior art which employ such materials as gelatin and corn syrup dextrins.

Claims 7 and 8 are dependent upon Claim 36 and specify, respectively, that the capsule shall have a particle

size of between about 1 and 20 microns diameter and between about 1 and 5 microns diameter. These are the particle sizes which appellant has found to provide most desirable results.

Claim 37 is similar to Claim 36 but defines appellant's capsules as having a shell of a hydrophobic water-insoluble film-forming material produced by a condensation chemical reaction. These capsules are of the type produced by Example V of the specification. The claim further specifies that the liquid droplets comprise between about 23% and 80% by weight of the capsule. This type of product is particularly distinguished from the prior art.

Claim 38 is similar to Claim 37, except that it refers to the product produced by encapsulating by means of solidification of a plastisol or organosol in accordance with Example XIV of the specification. This type of product is particularly distinguished from the prior art.

Claim 39 is also similar to Claim 37, except that it defines the product produced by cooling hot molten non-aqueous film-forming material. This claim is exemplified by Examples XII and XIII of the specification. This type of product is in no way suggested by the prior art.

Claim 22 defines appellant's free-flowing powder of microscopic discrete rupturable capsules as comprising liquid droplets encapsulated within an outer shell of a non-ionizable

water-soluble film-former material which will rupture under pressure. The claim next defines the particularly unique feature of the appellant's invention which constitutes forming the shell directly by evaporation forces on the solvent of a film-former solution which comprises the continuous phase of suspended minute particles of an emulsion, the discontinuous phase of which emulsion comprises the liquid droplets. This feature clearly distinguishes over the Green patent which teaches a product in which spray drying is employed only to dry the aqueous phase of a dispersion which contains previously existing capsules.

Claim 23 is similar to Claim 22 except that it specifies that the liquid droplets comprise marking fluid droplets. It is capsules containing this type of fluid which have found most utility up to the present.

B. Record Copying Sheet Claims

Claim 14 defines appellant's record copying sheet as one having on at least a portion of one side a coating of a free-flowing powder of microscopic discrete capsules having a rupturable shell and containing within the shell a marking fluid capable of being liberated when the shells of the discrete capsules are ruptured upon being subjected to an external printing or marking pressure. The claim further specifies that the discrete capsules are those defined by Claim 36. It is a record copying sheet which is prepared from appellant's capsules which provides advantages over

sheets produced using capsules in accordance with the Green patent. Capsules produced in accordance with the Green patent are produced in aqueous dispersions and it is the aqueous dispersions which Green contemplates applying to the paper. The application of aqueous dispersions possesses many disadvantages, including the tendency of water to corrugate the paper and cause it to buckle or warp even when specially prepared expensive paper is employed. Appellant's capsules, on the other hand, are produced in the form of free-flowing dry powders and can be applied to paper in a number of binders which are not aqueous and, therefore, do not buckle, warp or corrugate the paper. The use of a non-aqueous binder is just not feasible when following the teachings of the Green patent. In the case of appellant's invention, on the contrary, it is not only feasible, but preferred. In view of the outstanding results achieved and the differences in the character of the capsules employed, it is submitted that this claim is clearly patentable over the prior art.

Claim 15 is similar to Claim 14 except that it specifies that the capsules are held to the sheet by a binder which is of a different substance from that forming the rupturable shell of the capsules. This claim particularly distinguishes from the Green patent.

Claim 16 is similar to Claim 15 except that it specifies that the sheet is made of paper.

Claim 17 is dependent upon 16 and specifies that the marking fluid comprises a colored transfer substance.

Claim 18 is dependent upon Claim 16 except that it specifies that the marking fluid comprises a colorless material forming a color when brought into contact with another substance.

Claim 19 is dependent upon Claim 16 but specifies that the marking fluid shall comprise a colorless dye-former capable of producing a color when in the presence of an acidic substance. This is also not in any way suggested by the Green patent.

Claim 20 is also dependent upon Claim 16 and specifies that the capsules shall have a diameter of between 0.1 and 70 microns.

C. Process Claims

Process Claim 30 is the process counterpart of product Claim 22 and is directed to appellant's novel process of producing first an emulsion of liquid droplets in a solution of a non-ionizable water-soluble film-former in which the film-former solution comprises the discontinuous phase of emulsion and is substantially insoluble in the liquid droplets. Next, the emulsion is suspended as minute particles in a gaseous atmosphere and by evaporation forces there is produced the free flowing powder of microscopic discrete capsules. The claim further specifies that the liquid droplets shall comprise between about 23 and 80% by weight of the capsules. This two step process clearly distinguishes from the 10 step process of the Green patent.

Claim 11 is dependent upon Claim 30 and specifies that the evaporation is accomplished by spray drying.

Claim 13 is dependent upon Claim 30 and specifies that the capsules which are produced shall have a diameter of between about 0.1 and 70 microns.

Claim 31 is more limited than Claim 30 and specifies that the liquid droplets are marking fluid droplets.

Claim 32 is dependent upon Claim 31 and specifies that the marking fluid comprises a colored material.

Claim 40 is directed to the appellant's process for producing free-flowing rupturable capsules by means of cooling small particles of an emulsion of a hot molten non-aqueous film-former to solidify the film-former and thereby provide a free-flowing powder of capsules. This claim is directed to the process of Examples XII and XIII of the application. The claim further specifies that the droplets shall comprise between about 23 and 80% by weight of the capsule-forming emulsion. This process is particularly different from anything suggested by the references. There is no drying at all involved in this process since, by definition, the film-former does not contain substantially any water. An emulsion of a liquid discontinuous phase and a continuous phase of a hot molten wax-type film-former is employed with the wax solidifying upon cooling to form the shell of microscopic rupturable capsules. This process is completely foreign to anything suggested by the references and is therefore submitted to be manifestly patentable.

Claim 33 is dependent upon Claim 30 and specifies that the capsules shall have a diameter of 0.1 to 70 microns.

Claim 41 is directed to the process of producing the capsules employing a film-former which becomes hydrophobic and water-insoluble as a result of undergoing chemical condensation. This type of process is illustrated particularly by Example V of the present specification, whereby a water-insoluble hydrophobic cross-linked urea formaldehyde polymer is formed to provide the capsule shell. The claim specifies that the liquid droplets comprise between about 23 and 80% by weight of the capsules. This process is not even remotely suggested by the references and the claim is, therefore, submitted to be clearly patentable.

Claim 42 is directed to appellant's process whereby the film-former is a plastisol or organosol as employed in Example XIV of the specification. In accordance with this process the emulsion, in which the continuous phase is a plastisol, is finely divided and heated to form a rigid plastisol coating and thereby to produce capsules in the form of a free-flowing powder. The claim specifies that the liquid droplets shall comprise between about 23 and 80% by weight of the capsules. This process is also thoroughly remote from the references and therefore submitted to be manifestly patentable.

For reasons which have been discussed, it is submitted that these claims clearly distinguish appellant's invention from the teachings of the prior art.

CONCLUSION

It is respectfully submitted that for the reasons discussed hereinabove, that the invention on appeal is entitled to patent protection and that the Primary Examiner's decision should be reversed.

This brief is submitted in triplicate.

Respectfully submitted,

Louis F. Reed
Attorney for Appellant

New York 5, New York
October 28 , 1960.

Norman Macaulay Application Serial No. 676,574
Appeal No. 39,169

APPENDIX

Claims on Appeal

7. A substantially dry free-flowing powder as defined by Claim 36 wherein the capsules have a particle size of between about 1 and 20 microns diameter.

8. A substantially dry free-flowing powder as defined by Claim 36 wherein the capsules have a particle size of between about 1 and 5 microns diameter.

11. A process defined by Claim 30, wherein the evaporation is accomplished by spray drying.

13. A process as defined by Claim 30, wherein the resulting capsules which are produced have a diameter of between about 0.1 and 70 microns.

14. A record copying sheet having on at least a portion of one side thereof a coating of a free-flowing powder of microscopic discrete capsules comprising a rupturable shell containing therein a marking fluid capable of being liberated when the shells of said discrete capsules are ruptured upon being subjected to an external printing or marking pressure, said microscopic discrete capsules being those defined by Claim 36.

15. A record copying sheet having on at least a portion of one side thereof a coating of microscopic discrete capsules comprising a rupturable shell containing therein a marking fluid capable of being liberated when the shells of said discrete capsules are ruptured upon being subjected to external pressure, said capsules being held to said sheet by a binder which is of a different substance from that forming the rupturable shell of said capsules, said microscopic discrete capsules being those defined by Claim 36.

16. Paper having coated on at least a portion of a surface thereof microscopic discrete capsules comprising a rupturable shell containing therein a marking fluid capable of being liberated when the shells of said discrete capsules are ruptured upon being subjected to external pressure, said capsules being held to said sheet by a binder which is of a different substance from that forming the rupturable shell of said capsules, said microscopic discrete capsules being those defined by Claim 36.

17. Paper as defined by Claim 16 wherein the marking fluid comprises a colored transfer substance.

18. Paper as defined by Claim 16 wherein the marking fluid comprises a colorless material forming a color when brought into contact with another substance.

19. Paper as defined by Claim 16 wherein the marking fluid comprises a colorless dye-former capable of producing a color when in the presence of an acidic substance.

20. Paper as defined by Claim 16 wherein the capsules have a diameter of between about 0.1 and 70 microns.

22. A free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer shell rupturable under pressure of film-forming material, said encapsulating outer shell being formed directly by evaporation forces on the solvent of a film-former solution which comprises the continuous phase of suspended minute particles of an emulsion, the discontinuous phase of which emulsion comprises the liquid droplets, said liquid droplets comprising between about 23% and 80% by weight of the capsules, and said encapsulating outer shell being formed from a non-ionizable water-soluble film-forming material.

23. A free-flowing powder of microscopic discrete rupturable capsules comprising marking fluid droplets encapsulated within an outer shell rupturable under pressure of film-forming material, said encapsulating outer shell being formed directly by evaporation forces on the solvent of a film-former solution which comprises the continuous phase of suspended minute particles of an emulsion, the discontinuous phase of which emulsion comprises the marking fluid droplets, said capsules being capable of being ruptured under pressure to release the encapsulated marking fluid, said liquid droplets

comprising between about 23% and 80% by weight of the capsules, and said encapsulating outer shell being formed from a non-ionizable water-soluble film-forming material.

30. A process for producing a free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell being formed directly by evaporation forces on the solvent of a film-former solution of a non-ionizable water-soluble film-former which comprises the continuous phase of suspended minute particles of an emulsion, the discontinuous phase of which emulsion comprises the liquid droplets and between about 23% and 80% by weight of the capsules, which process comprises producing an emulsion of the liquid droplets in a film-former solution in which the latter forms the continuous phase and is substantially insoluble in the liquid droplets, suspending minute particles of said emulsion in a gaseous atmosphere, and then subjecting said suspended emulsion particles to evaporation forces to produce said microscopic discrete capsules in the form of a free-flowing powder.

31. A process for producing a free-flowing powder of microscopic discrete rupturable capsules comprising marking fluid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell being formed directly by evaporation forces on the solvent of a film-former solution of a non-ionizable water-soluble film-former which comprises the continuous phase of suspended minute particles of an emulsion, the discontinuous phase of which emulsion comprises the marking fluid droplets and between about 23% and 80% by weight of the capsules, which process comprises producing an emulsion of the marking fluid in a film former solution in which the latter forms the continuous phase and is substantially insoluble in the marking fluid, suspending minute particles of said emulsion in a gaseous atmosphere, and then subjecting said suspended minute emulsion particles to evaporation forces to produce said microscopic discrete capsules in the form of a free-flowing powder.

32. A process as defined by Claim 31 wherein said marking fluid comprises a colored material.

33. A process as defined by Claim 40, wherein the resulting capsules have a diameter between about 0.1 and 70 microns.

36. A free-flowing powder of microscopic discrete rupturable capsules having a particle size of between about 0.1 and 70 microns diameter, said capsules comprising liquid droplets encapsulated within an outer shell rupturable under pressure, said liquid droplets being substantially insoluble in and incapable of dissolving said outer shell and comprising between about 23% and 80% by weight of said capsules, said outer shell having a thickness comprising from about one-tenth to one-third of the capsule diameter and comprising a material selected from the class consisting of a non-ionizable water-soluble film-former and a hydrophobic water-insoluble film-former.

37. A free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer shell rupturable under pressure, said liquid droplets comprising between about 23% and 80% by weight of the capsules, said encapsulating outer shell being formed of a hydrophobic water-insoluble film-forming material produced by a condensation chemical reaction.

38. A free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer shell rupturable under pressure, said liquid droplets comprising between about 23% and 80% by weight of the capsules, said encapsulating outer shell being formed from a hydrophobic water-insoluble film-forming material by solidification from heating.

39. A free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer shell rupturable under pressure, said liquid droplets comprising between about 23% and 80% by weight of the capsules, said encapsulating outer shell being formed from a hydrophobic water-insoluble film-forming material by cooling hot molten non-aqueous film-forming material.

40. A process for producing a free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell being formed from a hot molten non-aqueous film-former comprising the continuous phase of an emulsion, the discontinuous phase of which emulsion comprises liquid droplets comprising between about 23% and 80% by weight of the emulsion, which process comprises producing an emulsion of the liquid droplets in said hot molten non-aqueous film-former in which the latter forms the continuous phase and is substantially insoluble in the liquid droplets, suspending minute particles of said emulsion in a gaseous atmosphere, and cooling the suspended particles to solidify said film-former and produce microscopic discrete rupturable capsules in the form of a free-flowing powder.

41. A process for producing a free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell consisting of a hydrophobic water-insoluble material produced by the chemical condensation of the reactive constituents of the film-former dissolved in aqueous solution, said solution comprising the continuous phase of an emulsion, the discontinuous phase of which emulsion comprises liquid droplets comprising between about 23% and 80% by weight of the capsules, which process comprises producing an emulsion of the liquid droplets in said aqueous solution of film-former constituents, causing said film-former constituents to undergo chemical condensation about the liquid droplets, and thereby produce said microscopic discrete rupturable capsules in the form of a free-flowing powder.

42. A process for producing a free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell being formed of a plastisol film-former comprising the continuous phase of an emulsion, the discontinuous phase of which emulsion comprises liquid droplets comprising between about 23% and 80% by weight of the capsules, which process comprises producing an emulsion of the liquid droplets in said plastisol film-former in which the latter forms the continuous phase and is substantially insoluble in the liquid droplets, heating minute particles of said emulsion to thereby produce said microscopic discrete rupturable capsules in the form of a free-flowing powder.

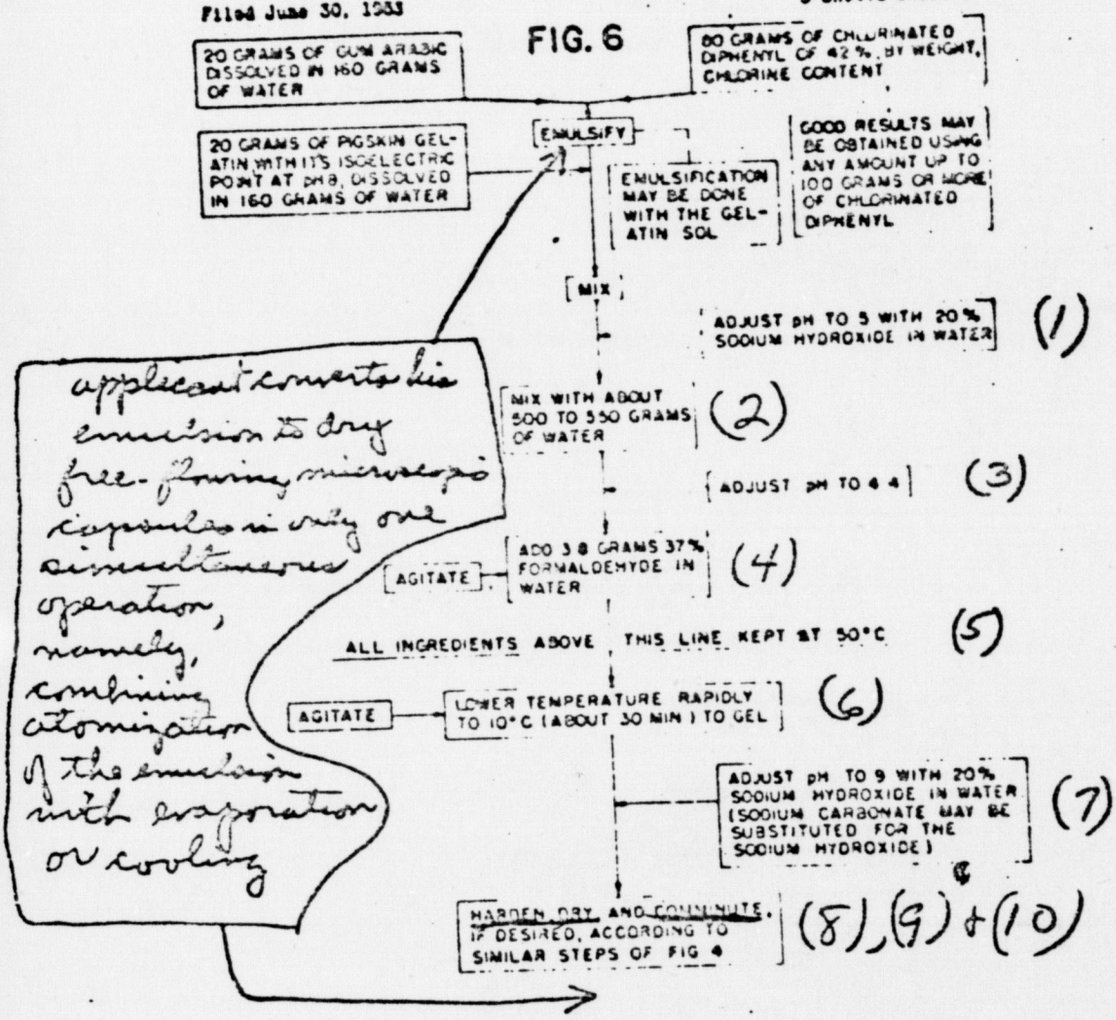
Exhibit "A"

July 23, 1957 B. K. GREEN ET AL 2,800,457

OIL-CONTAINING MICROSCOPIC CAPSULES AND METHOD OF MAKING THEM

Filed June 30, 1953 5 Sheets-Sheet 5

FIG. 6



applicant converts his emulsion to dry free-flowing microscopic capsules in only one simultaneous operation, namely, combining atomization of the emulsion with evaporation or cooling

INVENTORS
BARRETT K GREEN
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BY Hazard Bennett & Sturtevant

THEIR ATTORNEYS

POL-90
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U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications regarding this application should give the serial number, date of filing, and name of the applicant.

PAPER No. 13

Louis P. Reed
[illegible]
New York 5, N. Y.

Applicant: Norman Macaulay	
Ser. No. 670,574	MAILED
Filed Aug. 6, 1957	JAN 26 1961
For NOVEL MARKING PRODUCTS AND PROCESS	PAT. OFF. 25

Please find below a communication from the EXAMINER in charge of this application.

Robert C. Watson
Commissioner of Patents.

SHORTENED TIME FOR REPLY

Responsive to amendment filed June 5, 1959.

Upon reconsideration claims 7, 8, 11, 13-20, 30-33, 36 and 40-42 are found to be allowable.

Claims 22, 23 and 37-39 define the product in terms of its structure and not by the method of manufacture and are therefore improper. As pointed out at the top of page 20 of applicant's brief these claims were presented as alternative and will be cancelled upon allowance of the other type of product claims. Since the proper type of product claims have been found allowable these claims should be cancelled at this time.

The specification should be amended to make it consistent with the language of the claims. It is noted that there is no reference to "non-ionizable water-soluble film-former" in the specification.

The specification should be modified so that the brief summary of the invention and the descriptive matter are only as to the inventions to which the allowed claims are directed, i.e., since all the claims are limited to non-ionizable water-soluble film-former and hydrophobic water-insoluble film-former, All reference to other film-formers

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Ser. No. [illegible]

such as [illegible] casein and zein, for example, should be stricken from the specification.

Further prosecution on the merits of the case is closed in accordance with the decision of Ex parte Quayle, 1935 C.D. 11; 453 O.G. 213.

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS ACTION IS SET TO EXPIRE FEBRUARY 24, 1951.

Examiner

Mkatz:mrh

APPROVED
JAN 2 3 1951
SUPERVISORY EXAMINER

Paper No. 14

MAILED

FEB 6-1961

U. S. PATENT OFFICE
BOARD OF APPEALS

Appeal No. 391-69 1J

IN THE UNITED STATES PATENT OFFICE

BEFORE THE BOARD OF APPEALS

Ex parte Norman Macaulay

- - -

Application for Patent filed August 6, 1957, Serial No. 676,574. Novel Marking Products and Process.

Louis F. Reed for appellant.

In view of the Office action dated January 26, 1961 stating:

> "Further prosecution on the merits of the case is closed in accordance with the decision of Ex parte Quayle, 1935 C.D. 11; 453 O.G. 213."

The Appeal No. 391-69 has been removed from the Board's docket and the file returned to the Primary Examiner.

By Order of the Board of Appeals.

Nicholas Hahr
Administrative Officer
per fz

Louis F. Reed
20 Exchange Pl.
New York 5, New York

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IN THE UNITED STATES PATENT OFFICE DIV. 25

Applicant: Norman Macaulay
Serial No.: 676,574
Filed: August 6, 1957
For: NOVEL MARKING PRODUCTS AND PROCESS

Division 25

New York 5, N.Y.
February 22, 1961

Hon. Commissioner of Patents
Washington 25, D.C.

Sir:

AMENDMENT

In response to the Office Action of January 26, 1961, please amend the above-entitled application as follows:

Amend the title to read "NOVEL CAPSULE PRODUCTS AND PROCESSES FOR PRODUCING THE SAME".

In the Specification:

Page 2, line 3, cancel "of a marking fluid".

Page 6, line 16, cancel "of marking fluid" and replace with --having an outer shell of a material which is a non-ionizable water-soluble film-former or a hydrophobic water-insoluble film-former--.

Page 11, line 9, after "blendor." insert the following sentence: --In other words, the liquid droplets shall preferably comprise between about 23% and 80% by weight of the capsules.--

Page 13, line 1, before "water-soluble" insert --non-ionizable--; same line, after "the" insert --hydrophobic water-insoluble--; same line, insert a parenthesis before "organic" and after "solvent-soluble".

Cancel Example II starting at page 21, line 13 and ending at page 21, line 26.

Renumber Examples III through XVI as II through XV, respectively.

Page 25, line 22, cancel "IV" and replace with --III--.

Page 26, line 6 and page 28, line 12, cancel "VIII" and replace with --VII--.

In Table 2, page 29, cancel the third horizontal column which starts with "Gelatin" in the left-hand column.

In the Claims

Cancel and rewrite Claims 22 and 23 as:

14 ~~15~~. A free-flowing powder of microscopic discrete rupturable capsules as defined by ~~claim 35~~ 11 wherein the outer shell material is a non-ionizable water-so[illegible] film-former comprising a cellulosic material.

Cancel and ~~rewrite Claim 37 as:~~

~~16-44.~~ A free-flowing powder of microscopic discrete rupturable capsules as defined by ~~claim 36~~ 11 wherein the shell material is a hydrophobic water-insoluble film-former comprising a chemical condensation polymer.

~~Cancel and rewrite Claim 38 as:~~

~~17-45.~~ A free-flowing powder of microscopic discrete rupturable capsules as defined by ~~claim 36~~ 11 wherein the shell material is a hydrophobic water-insoluble film-former comprising a vinyl polymer.

~~Cancel and rewrite Claim 39 as:~~

~~18-46.~~ A free-flowing powder of microscopic discrete rupturable capsules as defined by ~~claim 36~~ 11 wherein the shell material comprises a fusible wax material.

~~Add the following claims:~~

22 ~~47~~. A free-flowing powder of microscopic discrete rupturable capsules as defined by claim ~~36~~ 11 wherein the liquid droplets comprise a marking fluid. cl 23

15 ~~48~~. A free-flowing powder of microscopic discrete rupturable capsules as defined by claim ~~43~~ 14 wherein the liquid droplets comprise a marking fluid. cl 16

17 ~~49~~. A free-flowing powder of microscopic discrete rupturable capsules as defined by claim ~~44~~ 16 wherein the liquid droplets comprise a marking fluid. cl 18

19 ~~50~~. A free-flowing powder of microscopic discrete rupturable capsules as defined by claim ~~45~~ 15 wherein the liquid droplets comprise a marking fluid. cl 20

21 ~~51~~. A free-flowing powder of microscopic discrete rupturable capsules as defined by claim ~~46~~ 20 wherein the liquid droplets comprise a marking fluid. cl 22

10 ~~52~~. A process for producing a free-flowing powder of microscopic discrete rupturable capsules comprising liquid droplets encapsulated within an outer rupturable shell of film-forming material, said encapsulating outer shell being formed directly by evaporation forces on the organic solvent of a film-former solution of a hydrophobic water-insoluble film-former in an organic solvent which comprises the continuous phase of suspended minute particles of an emulsion, the discontinuous phase of which emulsion comprises the liquid droplets, and between about 23% and 80% by weight of the capsules, which process comprises producing an emulsion of the liquid droplets in the film-former solution in which the latter forms the continuous phase and is substantially insoluble in the liquid droplets, suspending minute particles of said emulsion in a gaseous atmosphere, and then subjecting said suspended emulsion particles to evaporation forces to produce said microscopic discrete capsules in the form of a free-flowing powder. cl 11

REMARKS

Reconsideration of the application, as amended, is respectfully requested.

By the present amendment a more descriptive title has been introduced.

At page 2, line 3, the words "of a marking fluid" have been deleted since the invention is not limited to such materials.

Page 6, line 16 and page 13, line 1, have been amended in accordance with the Examiner's suggestion to introduce a specific reference to "non-ionizable water-soluble film-former" which is used in the claims and which is, of course, adequately supported by the specification and the allowed claims.

Page 11, line 9 has been amended to introduce the precise words supporting the limits of the liquid droplets comprising between about 23 and 80% by weight of the capsules, as set forth in many of the allowed claims. The basis for these proportions is found in the sentence preceding the insertion at page 11, lines 4 through 8.

In accordance with the Examiner's request, the specification has been amended to delete reference to film-formers which are not covered by the allowed claims. In this connection, the specification, particularly in view of the amendment to page 13, line 1, now defines the film-formers in accordance with the claims, namely, (1) non-ionizable water soluble film-formers or (2) hydrophobic water-insoluble film-formers. In view of this limitation, Example II and the third system under Table 2 on page 29, employing gelatin as a film-former, have been cancelled. The Examiner has suggested that casein and zein should be

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deleted from the specification apparently in the belief that they are not covered by the defined film-formers. It is submitted that casein and zein are justifiably retained in the specification. These materials are not water-soluble since they are soluble in water only in the form of their alkaline salts. Consequently, applicant contemplates these film-formers as hydrophobic water-insoluble film-forming materials. The specification and the allowed claims now both clearly distinguish over the references, particularly the Green patents which employed gelatin and materials capable of undergoing the "coacervation" phenomenon.

By the present amendment rejected claims 22, 23 and 37-39have been replaced by new claims 43 through 46. The new claims are free from the objection of defining the product in terms of the process of its manufacture. In this connection, it is noted that the first sentence of the third paragraph of the Office Action of January 26, 1961 sets forth the Examiner's objection to the rejected claims somewhat incorrectly. It is believed clear from the first full paragraph of the last page of the final rejection of March 3, 1960 that the Examiner's objection to the claims was that they did not define the product in terms of its structure, but rather in terms of the method of manufacture.

New claim 43 is intended to replace rejected claims 22 and 23. The claim is dependent upon allowed claim 36 and defines the shell material as being a cellulosic material. The claim is clearly free from the previous ground of rejection. Claims 37, 38 and 39 have been replaced by new claims 44, 45 and 46, respectively, all of which are dependent upon allowed claim 36 and define the film-former as a chemical condensation polymer, a vinyl polymer or a

fusible wax material, respectively. These claims are directed to the same subject matter as the rejected claims, but in addition to being dependent upon allowed claim 36, define theproduct in terms of its structure and composition and not the method of manufacture.

Several additional claims have been added. New claims 47 through 51, inclusive, are dependent upon claims 36 and 43-46, and are more limited than the parent claims in that they specify that the liquid droplets comprise a marking fluid. The present invention finds its greatest utility in providing copying material.

New claim 52 is a process claim drafted in language very similar to that of allowed process claim 30, merely differing in the use of a hydrophobic water-insoluble film-former, which is initially present in an organic solvent solution, instead of a non-ionizable water-soluble film-former as in claim 30. Claim 52 is clearly dominated by allowed product claim 36. This claim is adequately supported by this present specification, particularly original Examples Nos. VI and VIII, now Examples Nos. V and VII.

It is submitted that the application is now manifestly in condition for allowance and such action is respectfully requested.

Respectfully submitted,

Louis F. Real
Attorney for Applicant

POL-37

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U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications regarding this application should give the serial number, date of filing, and name of the applicant.

PAPER No. 16

Louis F. Reed
20 Exchange Place
New York 5, N. Y.

Applicant: Norman Macaulay	
Ser. No. 676,574	MAILED MAR 31 1961
Filed Aug. 6, 1957	
For NOVEL MARKING PRODUCTS AND PROCESS	PAT OFF 251

Please find below a communication from the EXAMINER in charge of this application.

Arthur W. Crocker
Acting Commissioner of Patents.

The changes hereinafter specified have been made in the application identified above in accordance with the provisions of Order Number 3141 of February 4, 1930, (Manual of Patent Examining Procedure 1302.04), which reads in part as follows:

> Other obvious informalities in the application may be corrected by the examiner, but such corrections must be in the form of an amendment, approved and signed by the Principal Examiner, placed in the file, and made a part of the record. A copy of the amendment is sent to the applicant. The changes specified in the amendment will be entered by the clerk in the regular way.

If these changes are not satisfactory to the applicant, an appropriate amendment may be proposed under the provisions of Rule 312, provided the printing of the specification has not begun at the time such amendment is ready for entry. To insure the consideration of such amendment for inclusion, it should be submitted on or before the date of remitting the final fee since the printing of the specification begins a few days thereafter.

The application has been amended as follows:

The title has been changed to read --RECORDING PAPER COATED WITH MICROSCOPIC CAPSULES OF COLORING MATERIAL, CAPSULES AND METHOD OF MAKING--.

The claims have been renumbered as follows:

Original	Issue	Depends On
30	1	
11	2	
13	3	1
31	4	1
32	5	
40	6	4
33	7	
41	8	
42	9	
52	10	
36	11	

USCOMM-DC-38025

Ser. No. 676,571 -2-

Original	Issue	Depends On
7	12	11
8	13	11
43	14	11
48	15	14
44	16	11
49	17	16
45	18	11
50	19	18
46	20	11
51	21	20
47	22	11
14	23	"
15	24	"
16	25	"
17	26	25
18	27	25
19	28	25
20	29	25

PROSECUTION OF THE MERITS IS CLOSED.

THE NOTICE OF ALLOWANCE WILL BE MAILED IN DUE COURSE.

MK
MKatz:mrh

R D Morris
Examiner

FORM PO-52
(10-60)

B 1077

Paper No.: 17

Serial No.: 176,574

REFERENCES CITED

The following references are of record in the patented file of this patent: EXAR 31 1961

UNITED STATES PATENTS

Name	Number	Date
Wallenmeyer	2,650,895	Sept. 1, 1953
Sandberg	2,711,375	June 21, 1955
Green	2,713,507	July 5, 1955
Hochberg	2,777,798	Jan. 15, 1957
Green	2,800,457	July 23, 1957
Green	2,800,458	July 23, 1957

FOREIGN PATENTS

Country	Number	Date

OTHER REFERENCES

133

USCOMM-DC 61429-P60

POL-85
6-30-60

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WASHINGTON 25, D. C.

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications respecting this application should give the serial number, date of filing, and name of the applicant.

NOTICE OF ALLOWANCE

The application for patent identified below has been examined and found allowable for issuance of Letters Patent.

	FILING DATE	SERIAL NO.	NO. OF CLAIMS ALLOWED	EXAMINER	DIV.
	08/06/57	676574	29	R. D. Nevius	25
APPLICANT	Macaulay, Norman, Niagara Falls, N. Y.			MAILED Apr. 7, 1961	
ASSIGNEE	Moore Business Forms, Inc.				
TITLE OF INVENTION	Recording paper coated with microscopic capsules of coloring material, capsules and method of making				

With the allowance of the application the final fee becomes due. This fee is thirty dollars ($30) plus one dollar ($1) for each claim allowed in excess of twenty (20) and must be paid within 6 months from the date of this notice. Failure to remit the final fee will result in the patent being withheld from issue.

As a convenience in remitting this fee, use of the enclosed Form POL-85a is suggested. The final fee will not be received from anyone other than the applicant, his assignee or attorney, or a party in interest as shown by the records of the Patent Office. If no entry appears in the space labeled "assignee," above, a form is enclosed relating to the address of the inventor(s) which requires your attention.

If it is desired to have the patent issued to an assignee or assignees, an assignment, together with the fee for recording the same, must be filed in this Office on or before the date of payment of the final fee.

The patent will be issued and forwarded within approximately two months after receipt of the final fee.

By direction of the Commissioner.

Louis F. Reed
20 Exchange Pl.
New York 5, N. Y.

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POL-85A
8-26-58

30.00 — 115
9.00 — 116

U. S. Department of Commerce
Patent Office

FINAL FEE TRANSMITTAL

This form is provided for convenience in transmitting final fees to the Patent Office. When properly completed it may be used in lieu of a formal transmittal letter. Respondents will note and fill in items numbered 1 thru 6 below. The Final Fee Receipt, in all cases, will be mailed to the address appearing in box at lower left of this form. If desired, use the reverse side of your Notice of Allowance for carbon copy when completing this form.

1. The COMMISSIONER OF PATENTS is requested to apply the accompanying fee to the case identified below, and deliver the patent as indicated.

MAIL ROOM OCT 9 1961 PATENT OFFICE

October 6, 1961
Date

Louis F. Read
Attorney, Agent or Applicant

NOTE—Final fees will not be received from other than the applicant, his assignee, or attorney, or a party in interest as shown by the records of the Patent Office. Final fees will not be applied to pending applications.

	FILING DATE	SERIAL NO.	NO. OF CLAIMS ALLOWED	EXAMINER	DIV.
	03/06/57	676574	29	R. D. Herbst	25
APPLICANT	Macaulay, Norman, Niagara Falls, N. Y.				
				MAILED Apr. 7, 1961	
ASSIGNEE	Moore Business Forms, Inc.				
TITLE OF INVENTION	Recording paper coated with microscopic capsules of coloring material, capsules and method of making				
				Notice of Allowance Date	

2. DEFERMENT: (Indicate below if desired)

Please permit the three months deferment provided by Rule 314

3. FEE ENCLOSED

$39.00

4. Assignee: (If assigned and name does not appear in the corresponding space above)

OCT-12-61 2617 A-CK — 115 30.00
OCT-12-61 2618 A-CK — 116 9.00

MAILING INSTRUCTIONS

Note—The office will send the patent to the address entered in stub at left below unless you direct otherwise. Use the spaces provided to indicate any changes which affect the delivery of the patent.

5. Do not send the patent to the address listed below. Send patent to (check one)

☐ Patentee
☐ Assignee
☐ Associate Attorney (See specific authorization)
☐ Change of address—Attorney

The address of the person checked above is typed in Item 6 below.

6.

135

Filing Date	Serial No	Final Fee	Issue Date
08/06/57	676574	339	01/09/62

INVENTOR	Macaulay, Norman, Niagara Falls, N. Y.
ASSIGNEE	Moore Business Forms, Inc.
INVENTION	Recording paper coated with microscopic capsules of coloring material, capsules and method of making
PDL 39 Notification Regarding Request for Deferment	Issue of the above identified allowed application for patent has been deferred as requested.
	Louis F. Reed 20 Exchange Pl. New York 5, N. Y.

U. S. Department of Commerce

136

Patent Office

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BOSTON OFFICE
(MASSACHUSETTS BAR)
LAFAYETTE 3-7340

FREDERICK B. FISH
W. R. RICHARDSON

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EDGAR H. KENT
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FISH, RICHARDSON & NEAVE

20 EXCHANGE PLACE

NEW YORK 5, N. Y.

NEW YORK OFFICE
(NEW YORK BAR)
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CHARLES NEAVE
(1883-1931)

MAXWELL BARUS
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JOHN VAUGHAN GROMER
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LEE C. ROBINSON, JR.

ROGER R. PHILLIPS
ALBERT E. FEY
M. FRANK HERSHAM
DANIEL P. CHERNOFF

March 14, 1962

SOLICITOR

MAR 19 1962

U. S. PATENT Office

Hon. Commissioner of Patents,

Washington 25, D. C.

Sir:

Re: Patent No. 3,016,308	:	Request
M. Macaulay	:	for
Issued Jan. 9, 1962	:	Certificate
For: Recording Paper Coated	:	of
with Microscopic Capsules of	:	Correction
Coloring Material, Capsules	:	
and Method of Making	:	

The patent certificate for the above patent has been received but in checking for printer's errors, several significant errors have been noted.

Column 1, line 31, "bands" should be "hands".

Column 5, line 10 "particles" should be "particle".

Column 5, line 42, "hydropholic" should be "hydrophobic".

Column 7, line 11, "a" has been omitted before "colored".

Column 9, line 6, "by" should be "of".

Table 2, at columns 11 and 12, the horizontal lines beginning "Petroleum resin" and "Piccopale" should be presented as a single composition and not as two separate compositions as in the patent.

APPROVED

MAY 17 1962

FOR THE COMMISSIONER OF PATENTS

137

FISH, RICHARDSON & NEAVE

TO——Hon. Commissioner of Patents

FOLIO 2.

It is requested that a Certificate of Correction be issued.

Respectfully,

Louis J. Reed

Attorney for Patentee

LFR:rn

138

POL-208
(8-61)

ADDRESS ONLY
THE COMMISSIONER OF PATENTS
WASHINGTON 25, D. C.

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

#19

Louis F. Reed
20 Exchange Place
New York 5, N. Y.

COPY MAILED

MAY 14 1962

U. S. PATENT OFFICE
COMMISSIONER'S OFFICE

Re: Patent No. 3,016,308 :
Norman MacMillay :
Issued January 9, 1962 :
For: Recording Paper Coated : Request for Certificate
with Microscopic Capsules of : of Correction
Coloring Material, etc.

In response to your letter requesting issuance of a certificate of correction in the above-identified patent, you are advised that such certificate will be issued if you will return the patent to the Patent Office.

DAVID L. LADD,
Commissioner

By A. M. Moore
Solicitor

2/15/p

Mr. A. W. Moore

BOSTON OFFICE
LAFAYETTE 3-7340

FISH, RICHARDSON & NEAVE

20 EXCHANGE PLACE
NEW YORK 5, N.Y.

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CHARLES NEAVE

SOLICITORS

REGISTERED MAIL

May 14, 1962 MAY 1 1962

U. S. PATENT OFFICE

Hon. Commissioner of Patents,

Washington 25, D. C.

Sir:

Re: Patent No. 3,016,308	:	Request
Norman Macaulay	:	for
Issued January 9, 1962	:	Certificate
For: Recording Paper Coated	:	of
with Microscopic Capsules of	:	Correction
Coloring Material, etc.	:	

Pursuant to the solicitor's letter of May 11, 1962, the Letters Patent is enclosed herewith so that the Certificate of Correction may be applied.

Very truly yours,

Louis F. Reed

LFR:rn

Enclosure

140

AO Form 120 (Rev. Oct. 1964)

In Re Patents

United States District Court

for the

#21

COMMISSIONER OF PATENTS,
Washington 25, D. C.

Buffalo

SIR:

In compliance with the Act of July 19, 1952 (66 Stat. 814; 35 USC 1350), you are advised that there was filed on the 25th day of January, 1972, in this court an action, No. Civ-1972-47, entitled:

Name Moore Business Forms, Inc., Plaintiff,

Address 900 Buffalo Avenue, Niagara Falls, New York

versus

Name Minnesota Mining and Manufacturing Company, Defendant,

Address 3389 Harlem Road, Cheektowaga, New York

brought upon the following patents:

	PATENT NO.	DATE OF PATENT	PATENTEE
1	3,016,308	Jan. 9, 1962	Plaintiff is owner - derived from an assignment from Norman Macaulay.
2			
3			
4			
5			

In the above-entitled case, on the day of , 19 , the following patents have been included by (insert amendment, answer, cross bill, or other pleading):

	PATENT NO.	DATE OF PATENT	PATENTEE
1			
2			
3			
4			
5			

In the above-entitled case the following decision has been rendered or judgment issued:

JOHN K. ADAMS, Clerk.

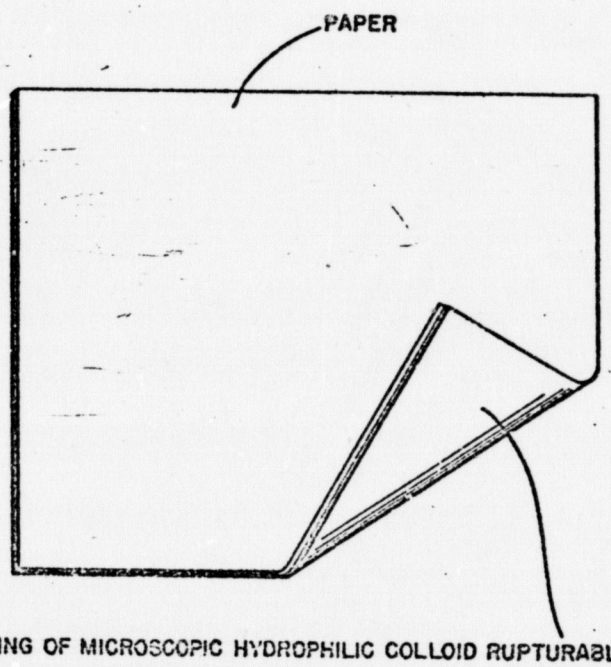
Date January 25, 1972 By , Deputy Clerk.

157

July 5, 1955 B. K. GREEN 2,712,507

PRESSURE SENSITIVE RECORD MATERIAL

Filed June 30, 1953



INVENTOR
BARRETT K. GREEN
BY Earl Reust
Justin A. Thurston
HIS ATTORNEYS

158

United States Patent Office 2,712,507 Patented July 5, 1955

2,712,507

PRESSURE SENSITIVE RECORD MATERIAL

Barrett K. Green, Dayton, Ohio, assignor to The National Cash Register Company, Dayton, Ohio, a corporation of Maryland

Application June 30, 1953, Serial No. 365,184

4 Claims. (Cl. 117—36)

This invention relates to manifold record material, and more particularly pertains to such record material which has a transfer coating thereon of microscopic gelled hydrophilic colloid capsules, each of said capsules consisting of a dense oil-impervious shell-like wall of film-forming colloid material deposited around a nucleus of an oily water-immiscible printing fluid by coacervate forces, said capsules being rupturable by printing or writing pressure applied to the record material so as to release said printing fluid for transfer to an underlying sheet.

The encapsulating material which encloses the oil droplets is a single gelled hydrophilic colloid material as contrasted with capsules made of a complex gelled gellable hydrophilic colloid material, which characterizes the encapsulating material of the microscopic oil-containing capsules with which the record material is coated, as disclosed in application for United States Letters Patent, Serial No. 365,198, which was filed on the same day as this application, by this applicant and Lowell Schleicher.

The record material of this invention also is distinguished from that disclosed in applicant Green's United States Patent No. 2,374,862, and applicant Green's and Robert W. Sandberg's United States Patents 2,548,366; 2,550,466; 2,550,467; 2,550,468; and 2,550,469, in that in the patents, instead of using microscopic oil-containing capsules in the transfer coating, the oily printing fluid was contained in droplet form in a continuous gelled hydrophilic colloid film.

In forming a continuous hydrophilic colloid film, there is a permeable condition set up whereby, even though the surface of the film is hardened by treatment that closes the surface pores, cracks may form through handling, or due to environmental conditions, which rupture the film. In such cracks the voids holding the oil are opened up because the cracks run straight through the voids. As the walls separating the voids in the film are somewhat permeable to the oil, oil may leak out, not only from the region of the cracks, but from uncracked portions of the film, leaving the film inadequate to perform its function.

In the present invention the microscopic capsules, although adherent to one another and to the paper, maintain their individuality so that if cracks are made by folding of the paper or otherwise, the cracks in the coating will run between the capsules and not through them. Also, in the present invention the microscopic capsules are made impermeable to the oil by a method disclosed and claimed in applicant's co-pending application for United States Letters Patent, Serial No. 365,196, filed the same day as this application. That method will be described in this application, insofar as applicable, but will not be claimed herein.

The manifold sheet of this invention, therefore, is superior to those shown in the patents to which reference has been made, insofar as shelf-life and durability are concerned.

Therefore, it is an object of this invention to provide a manifold sheet having a transfer film coating, on a surface thereof, which is composed of microscopic capsules of gelled hydrophilic colloid material, each of said capsules consisting of a dense oil-impervious shell-like wall of the colloid material deposited around a nucleus of an oily printing fluid by coacervate forces, and the capsules being present in such number as to be in substantial contiguity.

Inasmuch as the invention contemplates the use of color-reactant materials, which constitute the oil, or which form a part of the oil, it is another object of the invention to make such a manifold sheet in which the transfer coating is substantially colorless, but which will render colored marks upon sensitized receiving sheets.

With these and incidental objects in view, the invention includes certain novel features of structure and combinations of elements, a preferred form or embodiment of which is hereinafter described with reference to the drawing which accompanies and forms a part of this specification.

The drawing shows the manifold sheet of this invention in an enlarged and exaggerated form, so that the features may be discernible.

In the preferred embodiment of the invention there will be described a manifold sheet containing as the printing mark substance the compound 3,3 bis(p-dimethylaminophenyl) 6-dimethylamino phthalide, which is colorless and forms blue marks when coming into adsorption contact with a record material sensitized with acid claylike material such as attapulgite, or zeolite material, such as sodium aluminum silicate material, or such in which the sodium has been exchanged for hydrogen or some other metal ion, as disclosed in applicant's United States Letters Patents No. 2,531,186 and No. 2,641,557. As a secondary color-reactant in the oily printing fluid of the preferred embodiment there is provided a type of color reactant which oxidizes from a normally colorless form to a colored form when in contact with the clay materials just described, after the passage of some hours or days. This preferred compound is benzoyl leuco methylene blue. The phthalide compound, like all triphenyl methane dyes, tends to fade in time, but the secondary color reactant of the oxidizing type forms a color which is lasting. The phthalide compound reacts instantly to form a colored mark, to be supported later by the color of the oxidized secondary color reactant.

As the oily vehicle in which the color-reactants named above are carried, applicant has chosen for the preferred embodiment trichlorodiphenyl, the color reactants being used therein in amounts equal to several percent, by weight, of the total amount of the printing fluid.

As the encapsulating colloid material for the preferred embodiment, applicant has selected a gelatin, although other gellable film-forming hydrophilic colloids, such as agar-agar, will do.

The preferred method of forming the capsules includes the step of treating an aqueous sol of the colloid material having the oil emulsified therein, with a salt solution to cause the colloid material to deposit around the oil droplets, and then causing the colloid to gel. In making up the capsular material, one gallon of an oil-in-water emulsion of 20 parts, by weight, of trichlorodiphenyl containing the color reactants, and 100 parts, by weight, of a sol of 10%, by weight, of pigskin gelatin in water, is prepared, the emulsifying continuing until the drop size of the oil is from 2 to 5 microns. This material is kept at 50° centigrade to prevent the gelatin from gelling. With the temperature of the ingredients still kept at 50° C. coacervation then is induced by adding, slowly and uniformly, four-tenths of a gallon of 20%, by weight, of sodium sulphate in water. The uniform addition of this material is accomplished by continuous agitation.

ONLY COPY AVAILABLE

To gel the coacervate, the heated coacervate mixture is poured into 10 gallons of 7%, by weight, of sodium sulphate in water at 19° centigrade, with agitation. At this point the encapsulation of the oil with the gelled hydrophilic colloid material has taken place and the further steps are to put it in condition for use as intended. The material is filtered and washed with water, the temperature being kept below the melting point of the gelatin, to remove the salt. If desired, the filtered material is hardened by combining it with 2 gallons of a 37% solution of formaldehyde in water. This hardened mass is then filtered and washed to remove the residual formaldehyde. The resulting filter cake is adjusted to the proper water content by the addition of water or the removal thereof, by ordinary means such as centrifuging or spray drying, and the material is ready for use. As this material is intended for a paper coating composition, it is kept in aqueous suspension and applied directly to the paper, which is then dried, leaving the capsules adherent to the paper and to each other in a film.

If a portion of this fluid is sparsely dispersed in water and placed under a microscope, it will be seen to consist of microscopic capsules of the hydrophilic colloid material, the individual capsules being several microns in diameter and each containing a nucleus of oil. As the water content is decreased, the capsules tend to form aggregations, like bunches of grapes. When the material is of the right consistency, it is coated on paper by rollers, spray, brushes, or any other of the commonly used methods of coating paper, and allowed to dry. The material is of such a nature that the capsules are adherent to each other in the coating, and will adhere to the paper, without the addition of any other binder material.

For more details concerning the process of making the microscopic capsular material, reference is made to my co-pending application, Serial No. 365,106, regarding the process, to which attention has been drawn.

Other colorless adsorption color reactants which form color immediately on contact with acid clay-like material, such as the mentioned attapulgite, are malachite green lactone, which is 3,3 bis(p-dimethylaminophenyl) phthalide, and the ethyl and propyl homologues thereof, which form bluish green marks on the acid-like clay sensitized receiving sheet. Other comparable and equivalent materials are found in United States Patent No. 2,548,366, to which attention has been directed.

The material in the oil which produces the mark on the receiving sheet need not be a reactive material but may have an intrinsic color of itself, such as dissolved dyes, like Sudan III.

The oils which may be substituted for trichloro-diphenyl are any of the water immiscible oils, which are inert as to the other materials used in forming the capsules, such as petroleum fractions like paraffin oil, vegetable oil such as castor oil, and cottonseed oil, animal oils, such as sperm oil and lard oil, and any other various synthetic oils, such as methyl salicylate.

The coating material should be used in such quantity on the paper that when dried the coated area will be profusely supplied with the microscopic capsules, but such thickness need be no more than a fraction of a thousandth of an inch, because the size of the capsules is in terms of several microns. A four pound coating on a ream of paper 25 inches by 38 inches is satisfactory.

A sheet of ordinary writing paper, coated on one surface with the described coating composition laid with that coated surface on the attapulgite-sensitized surface of a receiving sheet, forms a manifold system which is responsive to very light printing or writing pressures, such as are ordinarily used in every-day printing and writing, so as to make clear and distinct marks on the receiving sheet, yet the coating is so durable that it will undergo rough handling without premature rupture of the capsules and is proof against the deleterious influences of the environment, either atmospheric or artificial.

The capsules may be rendered porous if the gelled material is allowed to dry without washing out the salt.

While the form of the invention herein shown and described is admirably adapted to fulfill the objects primarily stated, it is to be understood that it is not intended to confine the invention to the one form or embodiment herein disclosed, for it is susceptible of embodiment in various other forms.

What is claimed is:

1. A record material base sheet having on a surface thereof a coating consisting of a profusion of microscopic pressure-rupturable capsules having walls of gelled film-forming hydrophilic colloid material in substantial contiguity, each of the capsules consisting of an oily water-immiscible printing fluid as a central nucleus around which has been evenly deposited by coacervation forces a dense oil-impermeable shell-like coating of the colloid material, said capsules being rupturable by printing or marking pressures applied to the coated sheet.

2. Paper having coated on a surface thereof microscopic capsules having walls of gelled film-forming hydrophilic colloid material, the capsules being present in such number that they are in substantial contiguity, and each of said capsules consisting of an oily water-immiscible printing fluid as a central nucleus around which has been evenly deposited by coacervation forces a dense oil-impermeable coating of the colloid material, said capsules being rupturable by printing or marking pressures applied to the coated sheet of paper.

3. A sheet of paper having on a surface thereof a coating that is substantially colorless, said coating consisting of a profusion of pressure-rupturable microscopic capsules having walls of gelled film-forming hydrophilic colloid material in substantial contiguity, each of the capsules consisting of a dense shell-like oil-impermeable wall of the colloid material deposited about a central nucleus of a colorless oily water-immiscible printing fluid by coacervation forces.

4. The record material of claim 3 in which the oily printing fluid consists of a water-immiscible oil vehicle in which is carried a colorless color reactant which turns to a colored form on contact with paper sensitized by having thereon acid clay-like material.

References Cited in the file of this patent

UNITED STATES PATENTS

2,182,053	Taylor	Dec. 12, 1939
2,410,110	Taylor	Oct. 29, 1946
2,548,366	Green	Apr. 10, 1951
2,550,573	Green	Apr. 24, 1951

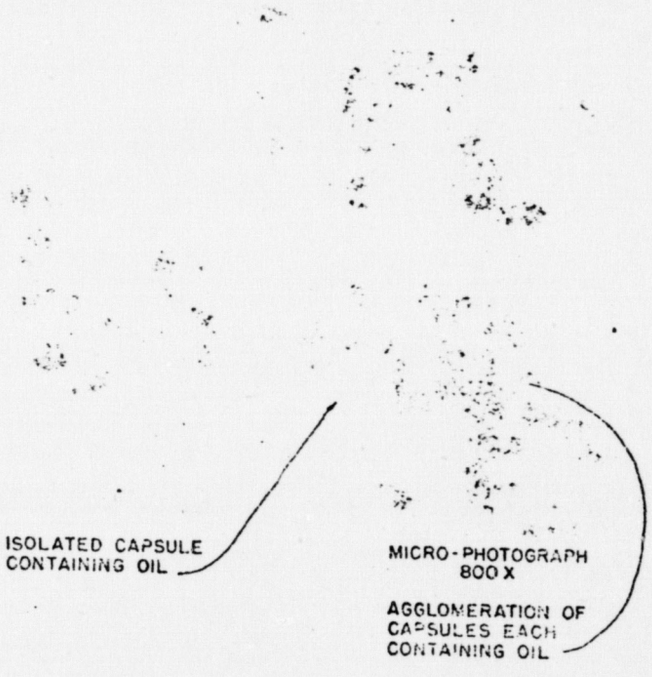
July 23, 1957 B. K. GREEN ET AL 2,800,457

OIL-CONTAINING MICROSCOPIC CAPSULES AND METHOD OF MAKING THEM

Filed June 30, 1953 5 Sheets-Sheet 1

FIG. 1

GUM ARABIC-GELATIN OIL-CONTAINING CAPSULES DISPERSED IN WATER.



INVENTORS
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LOWELL SCHLEICHER

BY Earl Brent
Justin S. Gordon
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July 23, 1957 B. K. GREEN ET AL 2,800,457

OIL-CONTAINING MICROSCOPIC CAPSULES AND METHOD OF MAKING THEM

Filed June 30, 1953 5 Sheets-Sheet 2

FIG. 2

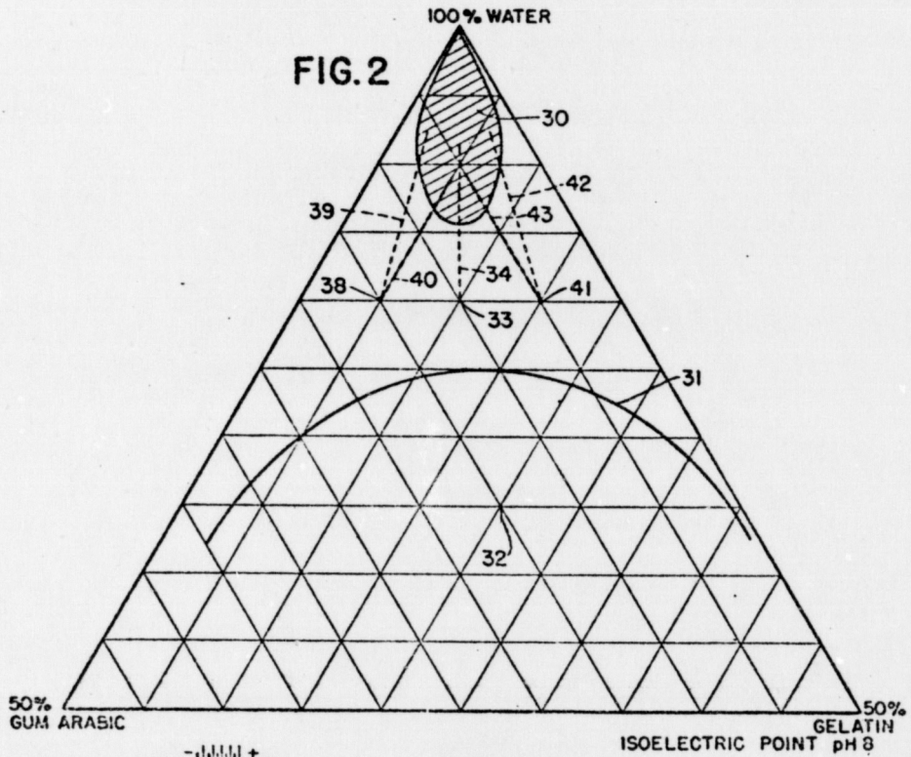
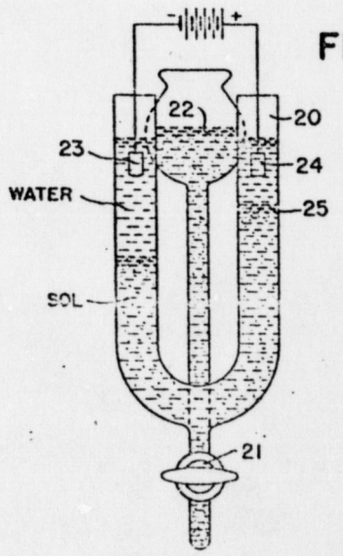


FIG. 3



INVENTORS
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Justin D. Compton
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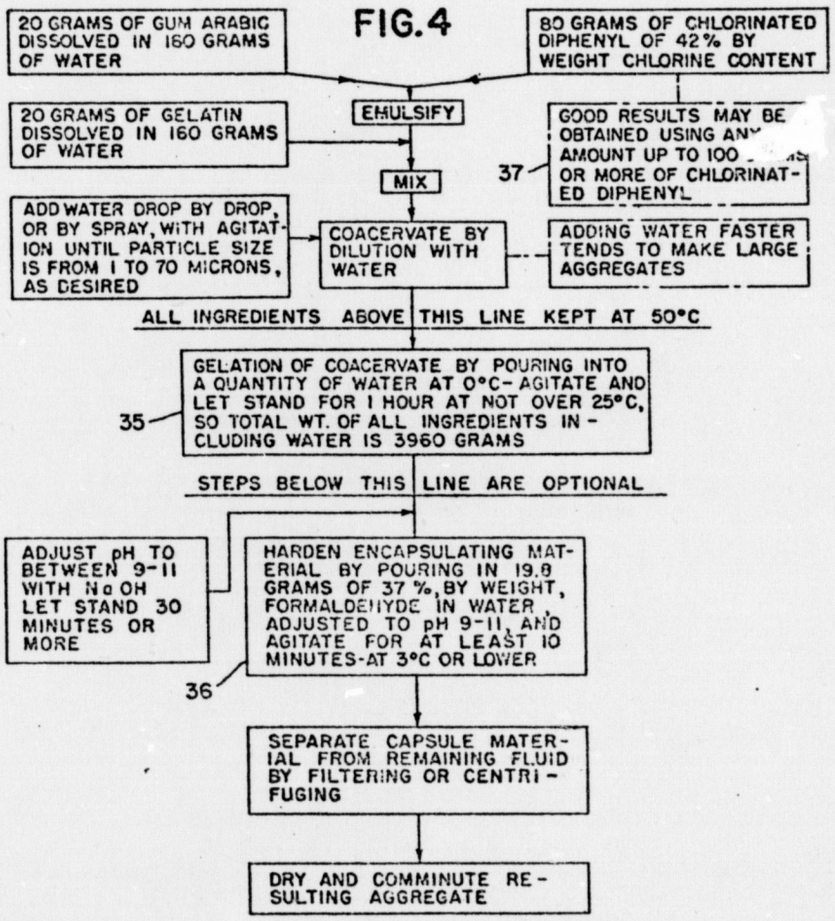
OIL-CONTAINING MICROSCOPIC CAPSULES AND METHOD OF MAKING THEM

Filed June 30, 1953 5 Sheets-Sheet 3

FIG. 4



INVENTORS
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Justin S. Compston
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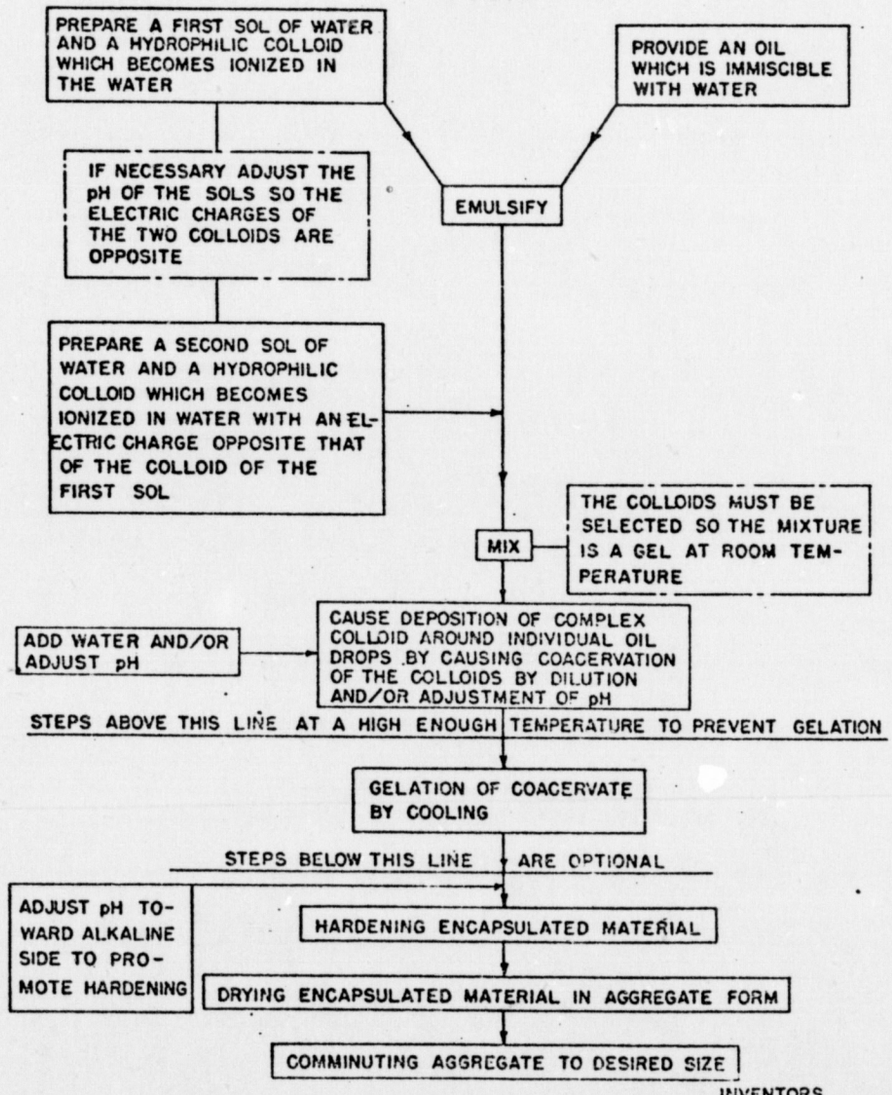
July 23, 1957 B. K. GREEN ET AL 2,800,457

OIL-CONTAINING MICROSCOPIC CAPSULES AND METHOD OF MAKING THEM

Filed June 30, 1953 5 Sheets-Sheet 4

FIG.5



INVENTORS
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BY Earl Berst
Justin S. Thurston

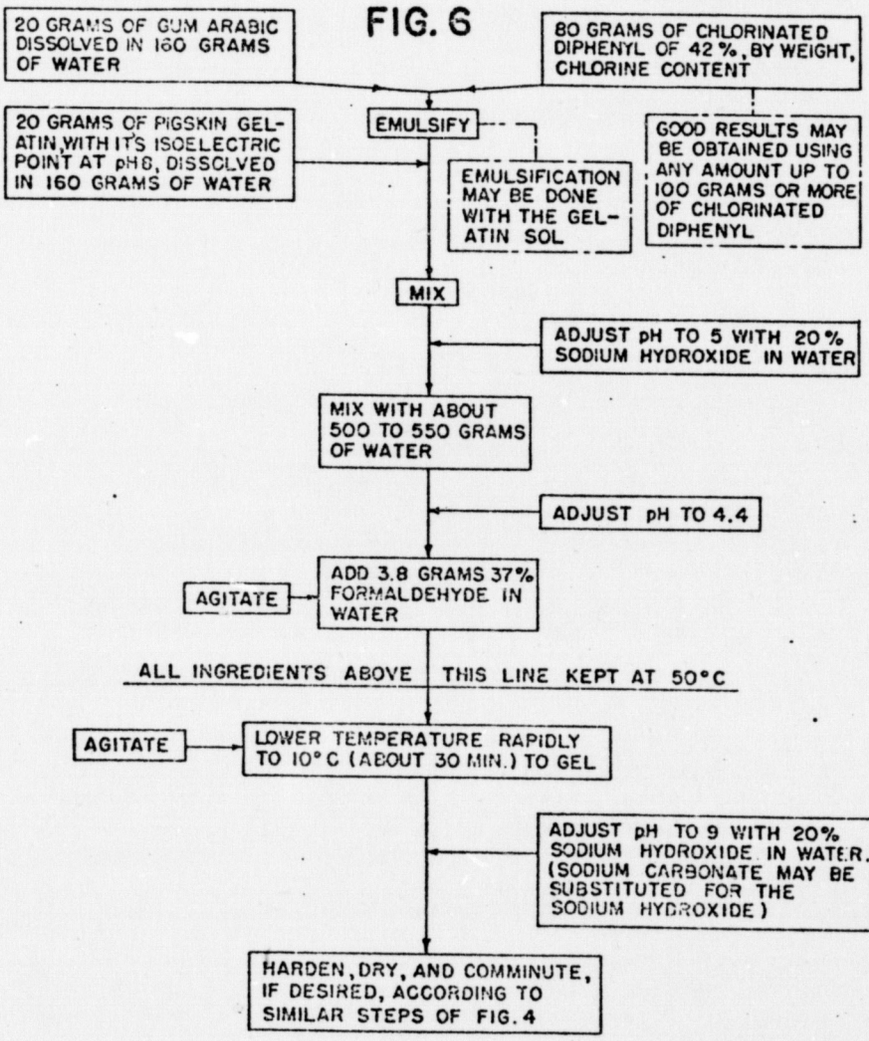
THEIR ATTORNEYS

July 23, 1957 B. K. GR:EN ET AL 2,800,457

OIL-CONTAINING MICROSCOPIC CAPSULES AND METHOD OF MAKING THEM

Filed June 30, 1953 5 Sheets-Sheet 5

FIG. 6



INVENTORS
BARRETT K. GREEN
LOWELL SCHLEICHER

BY Hearl Berest
Justin S. Thompson
THEIR ATTORNEYS

United States Patent Office 2,800,457 Patented July 23, 1957

2,800,457

OIL-CONTAINING MICROSCOPIC CAPSULES AND METHOD OF MAKING THEM

Barrett K. Green and Lowell Schleicher, Dayton, Ohio, assignors to The National Cash Register Company, Dayton, Ohio, a corporation of Maryland

Application June 30, 1953, Serial No. 365,105

11 Claims. (Cl. 252—316)

This invention relates to oil-containing microscopic capsules of complex hydrophilic colloid material and to a method of making them by coacervation.

In general, the capsules, which are microscopic oil-droplet-containing oil-impermeable cases formed of dense, gelled complex colloid material, are formed by causing deposition of complex colloid material around microscopic oil droplets as nuclei by a process of causing coacervation by dilution or adjustment of the pH to occur in a mixture of two different colloid sols in which the oil droplets are dispersed, and then gelling the complex colloid.

The mixture may be made by forming an aqueous sol of one colloid, emulsifying the selected oil therein, and mixing the emulsion with an aqueous sol of another colloid, or the two sols may be made and mixed and the oil emulsified therein.

The coacervation is caused by dilution and/or by adjusting the pH of the mixture. The gellable colloid materials used in the sols must be ionizable and exist in the mixture with opposite electric charges. This may be brought about by selection of the colloid materials or by adjusting the pH of the sol mixture in which the oil droplets are dispersed in the event one or both of the colloids are amphoteric.

If desired, after the gelation, any of the further steps of hardening the gelled material; separating the hardened gelled material from the remaining liquid; drying it; and comminuting it to the desired particle size, may be used.

Either one or both of the colloid materials should be gellable and used in such concentration that the coacervate complex colloid material is gellable. The process steps, down to the gelation step, are carried out with the ingredients at a temperature above the gel point of the colloid materials used, and gelation is brought about by cooling.

The finished product, before drying, may be used for coatings or films, as the capsules adhere together after drying, or the material may be cast into any wanted form.

If desired, after hardening and drying, the agglomerate mass of capsules may be comminuted to form fine granules of any desired size. The capsules, being so small and tending in the agglomerate form to cleave between the capsules, are not destroyed to any great extent by comminution of the mass.

The droplets of oil in the capsuless of the product are centrally located in the capsule and are protected from contact with the surrounding environment by a thick self-supporting tough shell-like film of the colloid materials. The encapsulating complex colloid material may be hardened and water-insolubilized to a point where the capsules are highly resistant to heat and moisture. The encapsulating film of a capsule may contain one or more droplets of oil, the droplets in the latter case maintaining their identity by persistence of the emulsion interface film.

By "oil" or "oils," as used in this specification, is meant any water-non-miscible fluid suitable for making oil-in-water emulsions. Included among the oils are those that occur naturally, such as olive oil; coconut oil; castor oil; fish oils; animal oils such as sperm oil; essential vegetable oils; mineral oils such as petroleum lubricating oil and kerosene, and xylene; and synthetic oils such as chlorinated diphenyl, methyl salicylate, etc. The oils may contain dissolved or dispersed material such as medicines, adhesives, dyes, and the like. In the case of dispersed material, it should be sufficiently fine to be colloidal in size.

By "ionizable hydrophilic colloid material" are meant substances such as gelatin; albumen; alginates, such as sodium alginate; casein; agar-agar; starch; pectins; carboxy-methylcellulose; Irish moss; and gum arabic.

As has been said, in order that coacervation may occur, the two kinds of colloid ions, as they exist in the mixture before coacervation, must have different electric charges. Some kinds of hydrophilic colloid ions in aqueous sols are negatively charged, regardless of the pH of the sol; some kinds are positively charged, regardless of the pH of the sol; and some are amphoteric, having an iso-electric point above which they are negatively charged and below which they are positively charged. The electric charge characteristics of a hydrophilic colloid under consideration may be determined by electro-phoresis in a manner to be described. In the event that one or both of the colloids used are amphoteric, the pH of the sols may be so adjusted that the colloid ions of the two kinds are of different electric charge. Amphoteric hydrophilic colloids of the same iso-electric point cannot be used.

In the process of coacervation, the complex colloid material deposits around the oil droplets to form the capsules.

One of the main uses for the capsules formed by this process is in the making of transfer films on manifold record material. The oil in the microscopic capsules so used would be of itself or contain a marking material which would be transferred to an underlying sheet by printing or marking pressures that rupture the capsules of the transfer film, to cause marks on said underlying sheet. Transfer films of rupturable type which contain oily droplets of marking fluid are disclosed in United States Patent No. 2,548,366, which issued on the application of Barrett K. Green, one of the applicants of this application, and Robert W. Sandberg, but such disclosed films are not composed of capsules. Transfer films such as those disclosed in the Green and Sandberg patent consist of a continuous film phase of hydrophilic colloid material having fluid droplets of oil dispersed therethrough. The aforesaid film affords some opportunity for escape of the fluid droplets because of the sponge-like texture of the colloid gel. Cracks in the films of the type disclosed in said patent will run right across the voids holding the oil, releasing the oil. Such cracks may be caused by folding the record material or may be caused by unusual environmental conditions.

The product of this invention makes transfer films much superior to those disclosed in the said patent, in that cracks in a film formed of the capsules of this invention do not run across the capsules, but run around them, so that the oil is not released by random cracks produced in the film. Moreover, the pore size of the complex colloid encapsulating film may be reduced during gelation and drying to hold the oil inside, as will be explained.

By the preferred method of manufacture of these capsules, the colloid material deposits around each oil droplet as a nucleus, forming a dense shell-like oil-impervious case with the oil nucleus at the center.

Because all films of gelled hydrophilic colloid material are to a degree molecularly porous because of the nature of gel structures, the capsules will be more or less porous according to the control exercised in forming

ANSWER:

(a) Officers of defendant from January 9, 1962

Irwin R. Hansen Treasurer, 1962-1963; Vice President

them. If the gelation step is performed rapidly, the pore size will be small and the capsules will retain, by sieve action, oils having relatively small molecules. If the gelation step is performed slowly, the pore structure of the encapsulating material will be coarser. The pore size of the capsules may be reduced further by a subsequent step in a high pH environment, as will be described, which makes the capsules harder, more heat resistant, and insoluble in water. If the capsules are used to hold marking fluids, small pores are desired, whereas, if the capsules are to be used for other purposes where slow release of the oil from the capsules is desired, larger pores would be preferred.

Other uses for the capsules involve the protection of oils against the deteriorating influence of the environment, to confine the odors of oils such as perfume oils, and to prevent the reaction of oils with other substances during handling or storage. Further uses of such capsules are to confine medicinal oils to prevent them from being tasted upon being swallowed by a patient, to protect them from the deleterious influence of various environments in which they may be stored, or to protect such from contamination with substances with which they may be mixed.

The capsules may be used in a liquid vehicle or may be dried in an oven and the resulting agglomerate material ground to form apparently dry granules. If desired, the fluid-suspended capsules may be spray-dried, in which event no comminution is necessary. In the dry granular form the capsules containing the fluid oil are handled and stored in the same manner as dry materials are handled and stored.

Therefore, it is an object of this invention to provide oil-containing microscopic capsules, the encapsulating material being a gelled hydrophilic colloid complex that is impervious to the oil and deposited evenly and densely about the oil as a nucleus.

It is another object of the invention to provide such capsules dispersed in a liquid.

It is an alternative object to provide such capsules in apparently dry form.

It is a further object of the invention to provide oil-containing capsules of hydrophilic colloid complex material in which the pore size of the encapsulating material has been controlled by controlling the environmental conditions of its manufacture.

Another further object of the invention is to provide such oil-containing capsules in which the encapsulating material has been hardened.

A still further object of the invention is to provide a process in which complex colloid material is deposited around oil droplets as nuclei, gelled, hardened and dried.

With further objects in view which will become apparent in the specification to follow, the invention includes the use of novel ingredients and processing steps, some of which are optional, described with reference to the drawings which accompany and form a part of this specification.

Of the drawings:

Fig. 1 is a reproduction of a micro-photograph of the capsules dispersed in a fluid, the magnification being about 800 diameters.

Fig. 2 is a ternary diagram showing the complex coacervation region of mixtures of gum arabic and gelatin aqueous sols without any artificial adjustment of the pH value, which is 4.5.

Fig. 3 shows an apparatus by which a colloid material's electric charge and iso-electric point may be determined.

Fig. 4 shows the steps of the process when no pH adjustment is made in the coacervating step.

Fig. 5 is a chart of the steps of the process in generalized form.

Fig. 6 is a chart of the steps of the process when adjustment of the pH is used for causing coacervation.

The process in general, as shown in Fig. 5, includes the steps of forming a first sol by dispersing one of the selected colloid materials in water; introducing the selected oil and forming an oil-in-water emulsion by beating or stirring; forming a second sol, similar to the first in concentration and amount, of the other selected colloid material and water; mixing the emulsion and the second sol; adjusting the pH of the mixture, if necessary, so that the ions of the two colloids have different electric charge; diluting with water, and/or changing the pH of the mixture until the complex coacervation takes place, all of the foregoing steps having been performed at a temperature above the gelation point of the colloids; cooling the resulting complex coacervate material to cause it to gel, as by subjecting it to an environment having a temperature below the gelation point of the coacervated complex; if desired, adjusting the pH of the material toward the alkaline side to promote hardening of the encapsulating material; stirring into the gelled material a solution of formaldehyde, or equivalent, in water to harden the encapsulating material; and finally, if desired, separating the capsules from the remaining liquid, drying them, and comminuting them if aggregated.

If gum arabic and gelatin are used, they, preferably, are used in the same concentration and amount to form the mixture. The amount of colloid used up as the emulsifier is so small as to be disregarded in computing the amounts of the colloid ingredients to be used in the mixture to be coacervated.

The iso-electric point of an amphoteric hydrophilic colloid material may be determined by forming an aqueous sol of it and testing it in the apparatus of Fig. 3 to determine the charge of the colloid ions. The thistle tube is filled with the sol 22, with the stop cock 21 closed. Water buffered to the pH of the sol then is introduced into the U-shaped portion 20 and the stop cock opened to admit the sol slowly until boundary layers are formed in both legs. Direct current is applied to the electrodes 23 and 24. If the colloid ions have negative charges, the separating interface line between the water and the sol will be higher in the leg containing the positive electrode than in the arm containing the negative electrode, as shown at 25, and vice versa. The iso-electric point may be ascertained by repeating the experiment with sols of various pH value until the boundaries remain level when electric potential is applied. Similarly, the natural charge of an ionized non-amphoteric hydrophilic colloid may be ascertained.

It is also necessary, in carrying out the process, to determine, by experiment, the dilution conditions under which the two selected kinds of colloids coacervate to form a colloid complex, and this may be done by testing sols containing the selected two colloids in various concentrations. This may be done experimentally for various pairs of colloids by preparing sols of them in various concentrations, mixing them, and diluting them slowly with water until a cloudy appearance indicates that complex coacervation has taken place. On standing, two layers will form, the coacervate colloid-rich layer still being liquid. Fig. 2 is a ternary diagram, the shaded area 30 at the top showing the region in which various concentrations of gum arabic and gelatin, having its iso-electric point at pH 8, coacervate. Such a diagram may be made for any two colloids with which it is desired to form the complex coacervate. Two sols are formed that are compatible. If the concentration of colloid material is too great, as in the region under curve 31, the sols will be incompatible and form two phases. The diagram is made by testing the mixtures of sols without the oil, as the oil will make the mixture opaque, so that the cloud point, indicating incompatibility or coacervation, cannot be seen.

If the mixture of colloids cannot be made to form a complex coacervate, the pH may be adjusted up or down

Donald O. Hambleton Assistant Secretary, 1970-1972

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to a point where experiments show that coacervation does take place upon dilution. Temperature also may be varied to a point where experiments show that coacervation takes place.

Considering the diagram of Fig. 2, more specifically, concentrations, of the particular colloids, below line 31 form incompatible mixtures; that is, the compatible sol mixture separates into two sols. As an instance of this, two sols are made, the first with 15 parts of gum arabic and 30 parts of water, and the second with 20 parts gelatin and 30 parts water. The light transmission of each sol is noted. If, now, these two sols are mixed together, the light transmission of the mixture is less than that of either sol alone, and, eventually, two layers will be formed, one being rich in one colloid and the other rich in the other colloid, showing the incompatibility of the sols and the unsuitability of the mixture for complex coacervation. The unsuitable mixture discussed is plotted approximately at 32. The light transmission may be roughly gauged by eye but is more accurately determined by an electrophotometer. Now, if two sols were made with the same gum arabic and gelatin, the first with 5 parts gum arabic and 80 parts water, and the second with 5 parts gelatin and 80 parts water, and mixed, the same clouding effect is noticed. In this case, however, a complex colloid is formed, by complex coacervation, forthwith and will separate out from the water by gravity, in time. In this case, the upper layer has practically no colloid material in it and will transmit light freely, whereas the lower layer is very cloudy. It is to be understood that there is no oil present in these tests.

A number of mixtures of low-concentration sols tested in the above manner will determine region 30, which is the coacervate region. Although the boundary of region 30 is given a sharp line, said boundary is not sharp, due to molecular weight variation in the particular polymers involved. However, it is readily ascertainable when the complete coacervation region has been entered. The region under line 31 and the enclosed region 30 having been determined, a point such as 33 is picked for making the mixture of sols for use in the process of this invention. Point 33 represents a sol mixture of 10% gelatin, 10% gum arabic, and 80% water. Dilution of this mixture with water added slowly produces the coacervation, the dotted line 34 representing the dilution necessary to take the mixture into the center of the coacervation region.

A ternary phase diagram, prepared as described, will furnish the necessary information for carrying out the process of this invention with any two selected colloid materials having in the mixture the necessary characteristics of different electric charge and gellability.

First, a specific example of the process will be given, when dilution only is used. A sol is made of 20 grams of gum arabic dissolved in 160 grams of water. Gum arabic in water always forms negative ions, it not being amphoteric, regardless of the pH. Into this is emulsified 80 grams of trichlorodiphenyl. A second sol of 20 grams of pork skin gelatin, having its iso-electric point at pH 8, and 160 grams of water is prepared, and this second sol is mixed with the emulsion. A volume of water then is added slowly to the mixture drop by drop, or by spray, with constant stirring until coacervation starts and is continued until the particle size of the oil droplets on which the coacervate material is deposited is as large as desired, the less water used the smaller the particle size. All of the foregoing steps are carried out with the ingredients at 50 degrees centigrade. The resulting coacervate mixture is poured into water at 0 degrees centigrade, enough water being used to bring the total weight of ingredients to 3960 grams. The mixture is agitated and thereafter is allowed to stand for an hour at not over 25 degrees centigrade. The formation of the capsules is now completed, and they may be used in suspension as a coating for surfaces or for other use as a fluid, or they may be dried and comminuted.

The capsular suspension resulting from the step of gelation, noted at 35 in Fig. 4, contains the coacervate capsules in usable form, the optional hardening step described above being used where it is desired to use heat to drive off the water or to render the capsules insoluble. If it is desired to use the capsules as a coating material for paper, the encapsulated particles at the step noted at 35 in Fig. 4 may be concentrated and applied to the paper and air-dried at a temperature below the melting point of the gel complex. Most of the water can be removed by centrifuging or filtering.

However, fast drying is desirable in coating paper, and the hardening step is provided as an optional step to permit the water to be driven off by heat.

The optional step to obtain a hardened capsular product from the coacervate suspensions requires the preferable step of adjusting the pH of the suspension of capsular material to between 9 and 11, by use of sodium hydroxide, and cooling the resulting slurry to zero degrees to 5 degrees centigrade; pouring in 19.8 grams of 37%, by weight, of formaldehyde in water adjusted to pH 9–11 with sodium hydroxide, and agitating for at least 10 minutes; and separating the resulting hardened capsules from the remaining liquid by filtering or centrifuging. Finally, if desired, the mass may be dried with heat (the hardening step preventing melting of the encapsulating material) and comminuted to the required granular size.

In filtering, first the free water is removed on a suction filter, then the filtrate mass is heated up to a maximum of 85 degrees centigrade to drive out the water which is bound in the gel network of the capsules. The water driven out of the gel, yet present in the mass, results in the formation of a smooth slurry of the capsules, which may be used as is while hot or filtered again. The hardened capsules suspended in water at the step marked 36 in Fig. 4 may be spray-dried in a hot environment to remove both the free water and the gel-bound water, or the spraying may be done after a first filtering step to remove the free water. If the slurry is allowed to cool after the first filtering and subsequent heating to drive out the water from the gel network, the water of the slurry will return to the gel network, leaving the mass as it was before heating. To avoid this return of the water to the capsule gel material, a dry hydrophilic colloid which preferentially will bind most of the water to itself is added to the hot slurry. With the materials used in the coacervate complex, high-viscosity polyvinyl alcohol added in the dry form will do, enough being used to attain the desired viscosity of the cooled material. The sol formed of the driven-off water and the added polyvinyl alcohol, or equivalent, will keep the material in fluid form on cooling.

The amount of oil used in proportion to the colloid ingredients of the complex may be varied greatly, as indicated at 37 in Fig. 4, where any amount up to 100 grams or more of the trichlorodiphenyl may be used with 40 grams of colloid material. Generally speaking, the more oil used, the thinner the encapsulating sheath will be, the oil drop size being maintained the same.

If the oil and the colloid material were used in equal amounts by weight, the capsule skin thickness would be greater. In addition to such thickening of the skin, aggregates of capsules are formed which seem to be encased in a mass of the colloid complex, whereas with the thinner-skinned capsules they agglomerate in bunches like grapes. Ordinarily, the aggregations and bunchings of the capsules are on a microscopic scale, but large enough aggregates to be barely visible to the unaided eye may be formed if sufficient dilution with water occurs in the coacervation step.

As examples of synthetic oils, mineral oils, vegetable oils, and animal oils which may be used in place of the

William L. McKnight Chairman of the Board and Chief Executive Officer, 1962-1966; Honorary Chairman of the Board, 1967-1972

trichlorodiphenyl used in the preferred embodiment of the invention may be mentioned methyl salicylate, petroleum oil, coconut oil, castor oil, and sperm oil. These oils were used in a proportion of 1 to 1, by weight, with the colloid materials. The hardening step when methyl salicylate is used must be at about pH 7, as at a pH above 7 there is chemical reaction between the sodium hydroxide and the methyl salicylate through the pore openings in the capsules. Whenever any such reaction is likely to occur between any of the ingredients, similar precautions should be taken.

The mixture of emulsion and sol need not contain equal parts, by weight, of the two colloids used, as will be evident from the diagram of Fig. 2. For instance, if the mixture contained 5% gelatin, 15% gum arabic, and 80% water, the dilution starting point would be at 38 on the diagram, and the coacervation region 30 could be obtained by diluting the mixture with water, in which event line 39 is followed. In this proportion of colloid material and water, the dilution could be made with a dilute gelatin sol. If a 5% gelatin sol were used, the line of dilution would be represented by broken line 40. If the starting mixture is at point 41, dilution with water would be along line 42, and dilution with a 5% gum arabic sol would be along line 43. From an observation of the diagram of Fig. 2, it will be obvious that less water dilution is needed when moving along center line 34 than when entering region 30 obliquely. The examples of starting mixtures represented at points 33, 38, and 41 are representative only and should not be deemed the only starting mixtures that could be used, as any convenient point between line 31 and region 30 could be a starting point.

Generally speaking, there should be no chemical reaction between the oil and the colloids, and the materials should be chosen with that point in mind.

Other agents than sodium hydroxide for adjusting the pH of the coacervate mixture are sodium carbonate and potassium hydroxide.

As was mentioned earlier, the encapsulated material could be either a printing fluid of an intrinsic color or a reactive ink that changes to a distinctive color when applied to sensitized record material. As examples of an oil with a color added may be mentioned Sudan III or Sudan IV dye in the before-mentioned trichlorodiphenyl. As examples of an oil with a colorless color reactant added may be mentioned 3,3 bis(p-dimethylaminophenyl)6 dimethylamino phthalide, or 3,3 bis(p-dimethylamino) phthalide in the trichlorodiphenyl.

With reference to Fig. 6, the process will be described where the mixture of sols and dispersed oil has the pH raised, before water is added, to a point where coacervation by dilution will not occur, and, after the addition of water, it is returned to the coacervate region by pH change.

Twenty grams of gum arabic is dissolved in 160 of water and emulsified with 80 grams of trichlorodiphenyl. This emulsion is mixed with a sol made of 20 grams of pigskin gelatin, with its iso-electric point at pH 8, and 160 grams of water. If desired, the emulsion may be made with the gelatin sol instead of the gum arabic sol, the sol which is used for making the emulsion being a matter of choice, or the sols may be mixed and the oil emulsified with the mixture. Good results may be obtained using up to 100 grams, or more, of the trichlorodiphenyl. The pH of the mixture of colloids and oil is about 4.5, and a complex coacervate will form if diluted according to the ternary diagram of Fig. 2. The process of dilution, when used, must be slow and uniform to insure proper deposition of the colloid material around the oil drops. To prevent this tedious dilution, the pH is adjusted to 5 or higher with 20% sodium hydroxide in water. The pH condition makes it impossible to cause complex coacervation of the colloids by the addition of the amount of water to be used. Next, 500 grams of water is introduced into the mixture, and the pH is slowly adjusted back to 4.5, which is in the complex coacervate range. Ten percent, acetic acid in water may be used for this pH adjustment. The 500 grams of water is a variable item, and, therefore, a larger or smaller amount may be used, depending on the oil drop size and the final aggregate size that is desired. In general, the larger the oil drop size the more water is needed, and the less water used the smaller will be the size of the capsule aggregates.

In all of the foregoing steps, the ingredients are kept at 50 degrees centigrade, and the mixture is being continuously agitated, but not so much so as to cause foaming. By adjusting the pH back to 4.5, the mixture is taken into the complex coacervate region, and the complex colloid is deposited around the oil droplets. To harden the capsules—that is to say, to harden the encapsulating material—3½ grams of 37% formaldehyde in water is added to the mixture with agitation. This last step of adding the formaldehyde is also done with the ingredients kept at 50 degrees centigrade. In order to complete the hardening action, a subsequent pH adjustment after gelation is necessary to bring the mixture to the alkaline side.

The mixture is next gelated by lowering the temperature to 10 degrees centigrade during a thirty-minute interval, with agitation, whereupon the complex encapsulating material forms a gel within which the oil droplets remain fluid. After this, the pH is adjusted to 9 with a 20% solution of sodium hydroxide in water. Sodium carbonate may be substituted for the sodium hydroxide, if desired.

This last form of bringing about complex coacervation is generally more efficient than that where large quantities of water are used to dilute the mixture, in accordance with the ternary diagram of Fig. 2. In this modified form of the process, wherein the complex coacervation is brought about by adjusting the pH, a more efficient use of the colloid material is made—that is to say, practically all of the colloid material goes into the making of the capsule walls—whereas, in the dilution form of causing complex coacervation, some of the complex colloid material exists apart from the oil droplets.

The capsular material, containing the oil droplets, made in accordance with Fig. 6, is of such consistency that it may be used directly to coat on paper to form a film in which each of the oil droplets is enclosed in its own hardened colloid capsule. This material may also be dried and comminuted, as was the case with the material made by the dilution form of the process. In fact, the material is practically the equivalent of that made by the dilution form of the invention except for the improvement noticed in the efficient utilization of the colloid material, and except for the fact that not so much water needs to be removed.

That the capsules actually retain the oil droplets has been proved in various ways. The dried capsular material was placed in a Soxhlet extractor with toluene and subjected to extraction for a week. The material was then removed and dried. Upon crushing the capsular material, oil was released. Paper upon which a film of the material containing 3,3 bis(p-dimethylaminophenyl)-6-dimethylamino phthalide in the oil droplets was similarly treated in the Soxhlet extractor. Upon removal and drying, it was used as a transfer sheet and placed over paper coated with attapulgite clay. It made marks on the clay-coated sheet when subjected to printing and writing pressures, that were as intense as marks made therewith before the extraction attempt. The same paper was put in an oven and kept there with an amount of unprotected oil equal to that in the paper. Whereas the unprotected oil evaporated in one day, there was no evidence of any loss of oil from the paper, even through left in the oven for ninety days at the same temperature.

While the invention, including the ingredients and the steps, has been fully outlined in the foregoing specifica-

Louis F. Weyand

Vice Chairman of the Executive Committee,
1962

St. Paul. Minnesota 55133

tion, the steps are capable of some modification in regard to temperature and amounts of ingredients used, and the ingredients themselves, of course, may be changed, as indicated earlier in the specification.

What is claimed is:

1. The method of making oil-containing microscopic capsules of complex hydrophilic colloid material, including the steps of providing an oil; mixing the oil with two compatible aqueous sols in which the oil is emulsified, the two sols containing, respectively, different hydrophilic colloid materials having opposite electric charges in the mixture, at least one of the colloids being gellable; causing coacervation of the colloid material by adding water to dilute the colloid mixture to an extent sufficient, in the absence of oil, to bring about a cloudiness in the mixture, to produce, by separation, a complex colloid rich portion and a colloid poor portion with said portions in equilibrium, whereby the complex colloid rich material deposits by coacervate forces around the individual oil droplets as nuclei, individually encapsulating each droplet, leaving the resulting capsules dispersed in the residual liquid consisting of the colloid-depleted portion of the mixture, the foregoing steps being carried out while maintaining the mixture at a temperature above the gelation point of the colloids therein; and gelling the encapsulating complex colloid material by cooling.

2. Microscopic oil-containing capsules made according to the method of claim 1.

3. The method of claim 1 in which the colloids used are gum arabic and gelatin.

4. Microscopic oil-containing capsules made according to claim 3.

5. The method of claim 1 in which the mixture of sols is made by emulsifying the oil in one of the aqueous sols and mixing the emulsion with the other aqueous sol.

6. The method of making oil-containing microscopic capsules of gelled complex hydrophilic colloid material, including the steps of forming an oil-in-water emulsion with an aqueous sol of a first ionizable hydrophilic colloid material as the external phase and a selected oil as the internal phase; mixing said emulsion with an aqueous sol of a second ionizable hydrophilic colloid material, at least one of the colloid materials being gellable, said colloid materials being used in such concentration that they are compatible in the mixture and so the complex to be made of them will be gellable, and said colloids being selected so as to have opposite electric charges in the mixture, the pH of the mixture being adjusted, to bring about such difference in electric charge; diluting the mixture uniformly with water, enough water being used to bring about, in the absence of oil, a cloudiness in the mixture to cause complex coacervation of the colloid materials and deposition of the complex material around the oil droplets as nuclei, all of the foregoing steps being performed at a temperature above the gel point of the sols; and cooling the resulting coacervate product to cause gelation of the resulting complex colloid encapsulating material.

7. Microscopic oil-containing capsules made according to the method of claim 6.

8. The method of making oil-containing microscopic capsules of gelled complex hydrophilic colloid material, including the steps of forming an oil-in-water emulsion with an aqueous sol of a first ionizable hydrophilic colloid material as the external phase and a selected oil as the internal phase; mixing said emulsion with an aqueous sol of a second hydrophilic colloid material, at least one of the colloid materials being gellable, said colloid materials being used in such concentration that they are compatible in the mixture and so the complex to be made of them will be gellable, and said colloids being selected so as to have opposite electric charges in the mixture; adjusting the pH of the mixture upwardly so that complex coacervation will not be brought about by water-dilution of the mixture; adding water in an amount which would have caused complex coacervation had not the pH been adjusted upwardly; adjusting the pH of the mixture downwardly to where it was, thus bringing about deposition of a complex coacervate material about the oil droplets, all of the foregoing steps being performed at a temperature above the gel point of the sols; and cooling the resulting product to cause gelation of the resulting complex colloid encapsulating material.

9. Microscopic oil-containing capsules made according to the method of claim 8.

10. The method of making oil-containing microscopic capsules of complex colloid material, including the steps of making an aqueous sol of gum arabic; making an aqueous sol of gelatin having its iso-electric point at pH 8; dispersing in either sol a water immiscible oil; mixing the resulting emulsion and the other sol together; and causing the colloid materials to form a complex coacervate, by dilution of the mixture with water to bring it into area 30 of Fig. 2 of the drawings, which coacervate deposits around the oil droplets, all the foregoing steps being carried out at a temperature above the gel point of the ingredients; and lowering the temperature until the complex colloid material around the oil droplets gells.

11. Microscopic oil-containing capsules made according to the method of claim 10.

References Cited in the file of this patent

UNITED STATES PATENTS

2,183,053	Taylor	Dec. 12, 1939
2,410,110	Taylor	Oct. 29, 1946

FOREIGN PATENTS

454,386	Germany	Jan. 6, 1928
514,047	Great Britain	Oct. 30, 1939

OTHER REFERENCES

Bungenberg: Chemical Abstracts, vol. 46, February 25, 1952, p. 1605.

Basu: Science, vol. 115 (1952), pp. 544 to 545.

Harry Heltzer 1965-1972 3M Center
St. Paul, Minnesota 55133

UNITED STATES .ATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,800,457 July 23, 1957

Barrett K. Green et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 42, after "provide" insert --microscopic--; column 7, line 56, after "160" insert --grams--.

Signed and sealed this 17th day of September 1957.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

Minnesota Mining and Manufacturing AB

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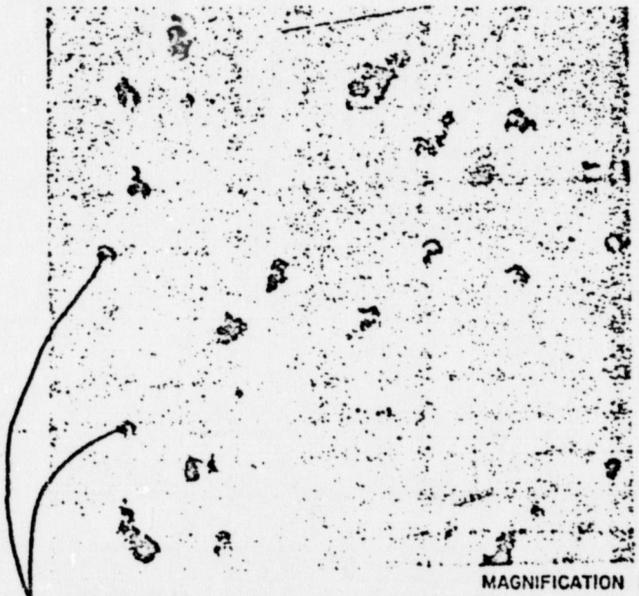
July 23, 1957 B. K. GREEN 2,800,458

OIL-CONTAINING MICROSCOPIC CAPSULES AND METHOD OF MAKING THEM

Filed June 30, 1953 4 Sheets-Sheet 1

FIG. 1

MICROSCOPIC OIL-CONTAINING CAPSULES OF GELLED HYDROPHILIC COLLOID MATERIAL



MAGNIFICATION 800X

GELATIN CAPSULES CONTAINING TRICHLORODIPHENYL DROPLETS, THE CAPSULES BEING SPARSELY DISPERSED IN WATER TO SHOW INDIVIDUALLY

INVENTOR
BARRETT K. GREEN

BY Earl Berndt
Justin S. Thurston
HIS ATTORNEYS

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Minnesota de Espana, S.A.
Minnesota Mining and Manufacturing AB

(a) State fully the reasons that are the basis for

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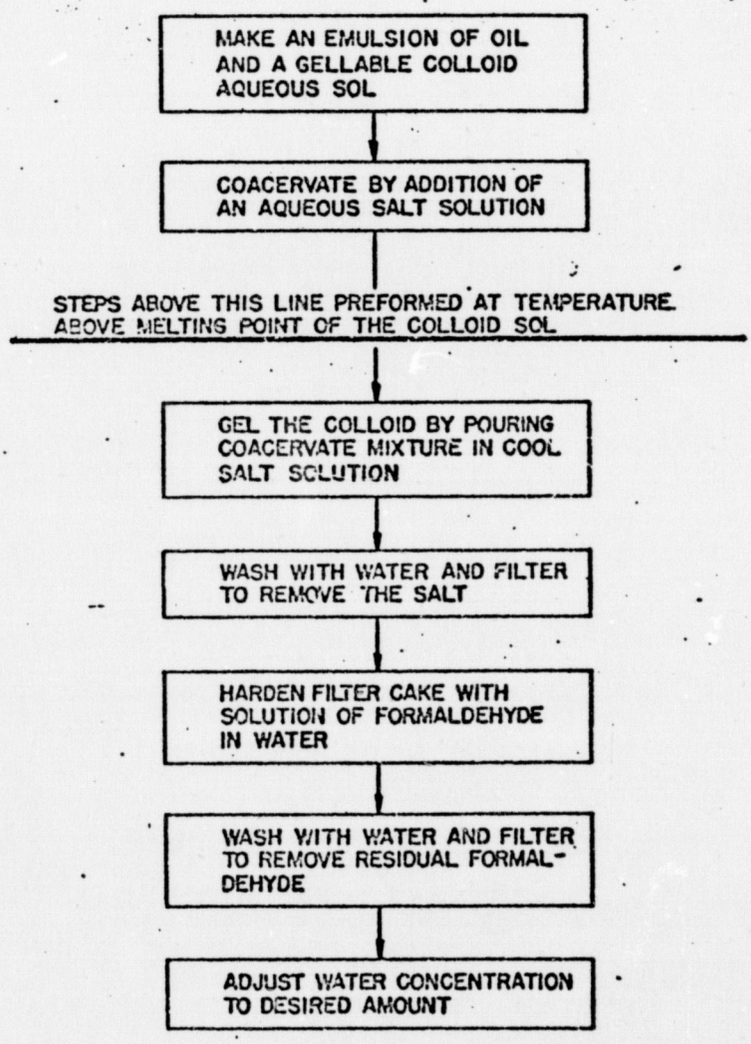
July 23, 1957 B. K. GREEN 2,800,458

OIL-CONTAINING MICROSCOPIC CAPSULES AND METHOD OF MAKING THEM

Filed June 30, 1953 4 Sheets-Sheet 2

FIG. 2



INVENTOR
BARRETT K. GREEN
BY Pearl Berest
Justus S. Compton
HIS ATTORNEYS

Interrogatory No. 4

(a) State fully the reasons that are the basis for

Those of the listed patents designated by either a single

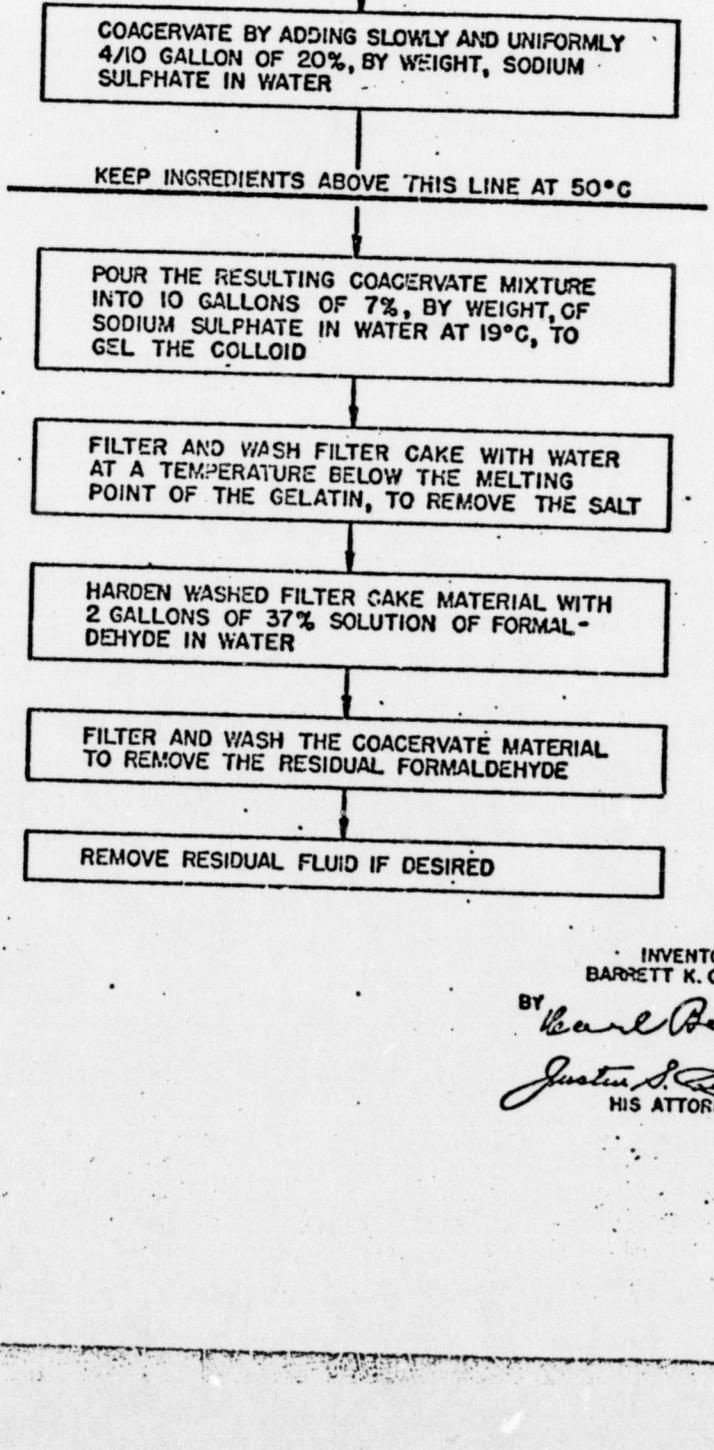
173

July 23, 1957 B. K. GREEN 2,800,458

OIL-CONTAINING MICROSCOPIC CAPSULES AND METHOD OF MAKING THEM

Filed June 30, 1953 4 Sheets-Sheet 3

FIG. 3



INVENTOR
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Justus S. Simpson
HIS ATTORNEYS

Those of the listed patents designated by either a single

July 23, 1957 B. K. GREEN 2,800,458

OIL-CONTAINING MICROSCOPIC CAPSULES AND METHOD OF MAKING THEM

Filed June 30, 1953 4 Sheets-Sheet 4

FIG. 4

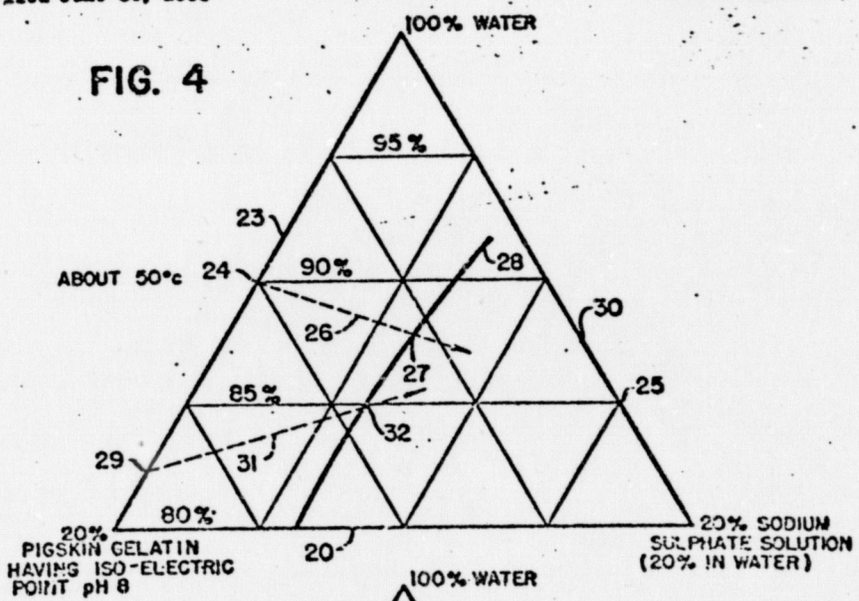
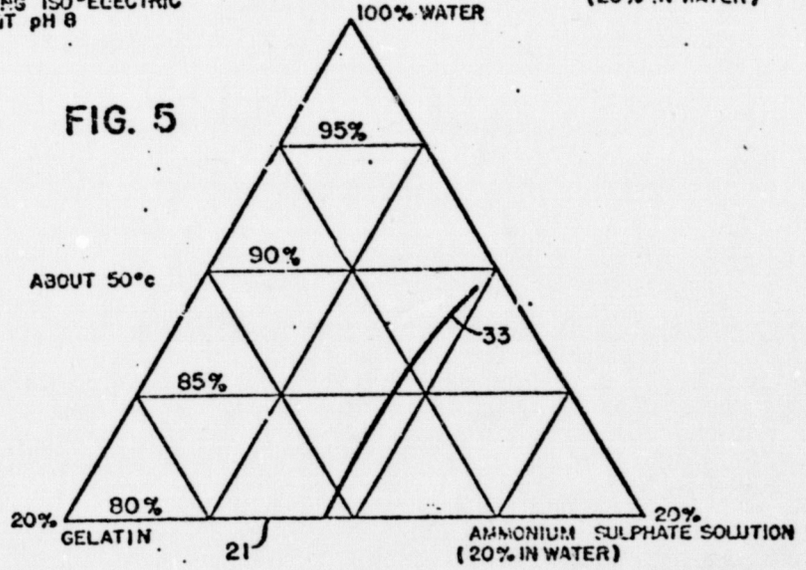


FIG. 5



INVENTOR
BARRETT K. GREEN
BY Earl Barrett
Justus S. Lamb & Co.
HIS ATTORNEYS,

.175

United States Patent Office

2,800,458
Patented July 23, 1957

2,800,458

OIL-CONTAINING MICROSCOPIC CAPSULES AND METHOD OF MAKING THEM

Barrett K. Green, Dayton, Ohio, assignor to The National Cash Register Company, Dayton, Ohio, a corporation of Maryland

Application June 30, 1953, Serial No. 365,106

14 Claims. (Cl. 252—316)

This invention relates to oil-containing microscopic capsules of a gelled hydrophilic colloid material and to a method of making them by salt-concervation.

The microscopic oil-impermeable capsules, made in an aqueous medium, are several microns in diameter, and each contains, as a central nucleus, oil surrounded by a relatively and uniformly thick encapsulating wall of the gelled colloid material. If the capsules are dispersed in a great deal of water they may exist individually, but if the free water is removed the capsules tend to agglomerate like bunches of grapes until the mass becomes adherent and more or less solid.

By the process steps to be described, the colloid encapsulating material is rendered impermeable, as far as the oil is concerned, so that it cannot escape until the capsule is ruptured. In this way the oil is contained protected against environmental and other deleterious influences. In the event the free water is removed, the capsules may be treated as solid material even though more than 50% of the weight of the mass may be oil in liquid form. If desired, the capsules may be hardened and rendered insoluble so that the free water may be driven off by heat, the dried material being immune to the destructive influence of water and other equivalent solvents.

The oils which may be used in the process are the water-immiscible oils which are inert as to the encapsulating material and which may be emulsified with an aqueous sol of the particular hydrophilic gellable colloid used. Among such oils are the mineral oils such as petroleum fractions; animal oils such as sperm oil; fish oils such as halibut liver oil; vegetable oils such as cotton seed oil, corn oil, castor oil, and coconut oil; essential oils from plants, and synthetic oils such as methyl salicylate and chlorinated diphenyl.

Among the gellable hydrophilic colloid materials may be mentioned gelatin and agar-agar.

In the oil, that is used to form the droplets which are surrounded by the encapsulating material, may be dissolved various selected materials, or dispersed solid material of colloidal size, such added substances, of course, being inert to the other ingredient materials. Among such finely divided solid substances may be mentioned dyes such as are used in making inks, solid chemical reactant substances which will be described, medicines, perfumes, and other materials which it is desired to have protected from the environment or which it is desired to have isolated for other reasons. Among substances which may be dissolved in the oil may be mentioned oil-soluble dyes, adhesives, oil-soluble vitamins, and the like.

Among the most important uses for such material in an aqueous dispersion is as a paper coating composition which forms a transfer film. The oil in the microscopic capsules so used would be of itself or contain a marking material which would be transferred to an underlying sheet by printing or marking pressures that rupture the capsules of the overlying transfer film, to cause said marks on the underlying sheet. Transfer films of rupturable type which contain oily droplets of marking fluid are disclosed in United States Patent No. 2,548,366, which issued on the application of Barrett K. Green, this applicant, and Robert W. Sandberg, but such disclosed films are not composed of capsules. Transfer films such as disclosed in said patent consist of a continuous film phase of gelled hydrophilic colloid material having fluid droplets of oil dispersed therethrough. The aforesaid continuous film affords some opportunity for escape of the fluid droplets because of the sponge-like texture of the colloid gel film surrounding the voids which hold the oil. Cracks in the films of the type disclosed in said patent will run right across the voids which hold the oil, releasing the oil. Such cracks may be caused by folding or rough handling of the material, or may be caused by unusual environmental conditions.

The product of this invention makes transfer films superior to those disclosed in said patent, in that cracks in the film formed by the capsular material of this invention do not run across the capsules, but around them, so that the oil is not released by random cracks produced in the film. Moreover, the pore size of the hydrophilic colloid encapsulating film may be reduced during gelation and drying to render the encapsulating film impermeable to the oil inside, as will be explained.

Because all films of gelled hydrophilic colloid material are to a degree molecularly porous because of the nature of gel structures, the capsules will be more or less porous according to the control exercised in forming them. If the gelation step is performed rapidly the pore size will be small and the capsules will retain, by sieve action, oils having relatively small molecules. If the gelation step is performed slowly the pore structure of the encapsulating material will be coarser. The hardening step is carried out in a high pH environment, as will be described, which makes the capsules harder, more heat resistant, and insoluble in water. If the capsules are used to hold marking fluids, small pores are desired, whereas if the capsules are to be used for other purposes where slow release of the oil from the capsules is desired, larger pores would be preferred. The process is flexible to achieve either condition.

If the capsules are to be dried, they may be dried in an oven and the resulting agglomerate material ground and washed to remove the oil which escaped during grinding, to form apparently dry granules or, if desired, the fluid-dispersed capsules may be spray dried, in which event no comminution or washing is necessary. In the dry granular form the capsules containing the fluid oil are handled and stored in the same manner as other dry materials are handled and stored.

Therefore, it is an object of this invention to provide microscopic capsules of a gelled hydrophilic colloid material each having a central oil nucleus.

It is another object of the invention to provide such capsules dispersed in a fluid.

It is an alternative object to provide such capsules in outwardly dry form.

It is further an object of the invention to provide microscopic oil-containing capsules of hydrophilic gelled colloid material in which the pore size of the encapsulating material was controlled by the conditions of its manufacture.

Another further object of the invention is to provide such oil-containing capsules in which the encapsulating material has been hardened.

With further objects in view which will become apparent in the specification to follow, the invention includes the use of novel ingredients and processing steps, some of which are optional, described with reference to the drawings which accompany and form part of this specification.

(2) By reference to specific parts of the specifi-

Of the drawings:

Fig. 1 is a reproduction of a micro-photograph of the capsules dispersed in a great amount of water, the magnification being about 800 diameters.

Fig. 2 is a block diagram showing the steps followed in making the gelled and hardened colloid capsules, this figure showing the process in general without the specific recitation of ingredients and amounts of ingredients.

Fig. 3 shows the method in more specific form, with gelatin and trichlorodiphenyl as the ingredients, and with sodium sulphate as the salt.

Fig. 4 is a tertiary diagram showing the coacervation region of a sol of gelatin in water, using sodium sulphate as the salt.

Fig. 5 is a ternary diagram showing the coacervation region of a sol of gelatin in water, using ammonium sulphate as the salt.

Referring to Fig. 2, the process, in general, includes the first step of forming an emulsion of oil and a gellable colloid aqueous sol. This is made by dispersing the colloid in water, adding the oil and forming an emulsion by stirring. Next, after having determined the coacervate region of the sol, by making a diagram as shown in Figs. 3 and 4, as well be described, a coacervate is formed by the addition of a proper amount of an aqueous solution of a suitable coacervating salt. In order that the colloid will not gel prematurely the foregoing steps are performed at a temperature above the melting point of the colloid sol. Thereafter, the colloid is gelled by pouring the coacervate mixture into a cool solution of the same salt which was used for the coacervation, causing the colloid deposited around the individual oil droplets to gel. This gelled colloid capsular mass is washed with water and filtered to remove the salt. If it is desired to harden and make the capsular material hard and insoluble, the filter cake is treated with a solution of formaldehyde. According to what use is to be made of the finished material, the free water is adjusted to the desired concentration, or the free water is removed entirely.

The preferred form of the invention, shown step by step in Fig. 3, utilizes gelatin, preferably high quality pig skin gelatin which has its iso-electric point at pH 8. Inasmuch as the finished encapsulated material will find an important use in the making of coating compositions which will form a transfer film on record material, such as paper, the preferred oil used is trichlorodiphenyl which is relatively non-volatile, inert, and which can be obtained in a colorless and pure form. Into this trichlorodiphenyl may be dissolved a colorless color-reactant such as the crystal violet lactone which is, as specified in the patent to which reference has been made, 3,3 bis(p-dimethylaminophenyl) 6-dimethylamino phthalide. The described phthalide compound has a white crystalline structure and, when dissolved to the extent of about 3%, by weight, in the trichlorodiphenyl and placed in contact with a sheet of paper sensitized with attapulgite, will turn to a dark blue color similar to crystal violet. When fluid-dispersed capsular material containing this oil is applied to a sheet and dried to form a transfer film, the capsules may be ruptured locally at points of printing and marking pressures to release the oil which will thereupon come in contact with the sensitized undersheet, as mentioned in said patent. In making up the preferred material, one gallon of an oil-in-water emulsion of 20 parts, by weight, of trichlorodiphenyl containing the phthalide and 100 parts, by weight, of a sol of 10%, by weight, of pigskin gelatin in water, is prepared, the emulsifying continuing until the drop size of the oil is from 2 to 5 microns. This material is kept at 50° centigrade to prevent the gelatin from gelling. With the temperature of the ingredient still kept at 50°, the coacervation then is induced by adding, slowly and uniformly, four-tenths of a gallon of 20%, by weight, of

sodium sulphate in water. During coacervation, the gelatin molecules are deposited uniformly about each oil droplet as a nucleus. The uniform addition of this material is accomplished by continuous agitation.

To gel the coacervate, the heated coacervate mixture is poured into 10 gallons of 7%, by weight, of sodium sulphate in water at 19° centigrade, with agitation. At this point the encapsulation of the oil with gelled hydrophilic material has taken place and the further steps are to put it in condition for use as is intended. The material is filtered and washed with water, the temperature being kept below the melting point of the gelatin, to remove the salt. If desired, the filtered material is hardened by combining it with 2 gallons of a 37% solution of formaldehyde in water. This hardened mass then is filtered and washed to remove the residual formaldehyde. The resulting filter cake is adjusted to the proper water content by the addition of water or the removal thereof, by ordinary means such as centrifuging or spray drying, and the material is ready for use. If this material is intended for paper coating composition it is kept in aqueous suspension and applied directly to the paper which is then dried leaving the capsules adherent to the paper and to each other in a film.

In determining under what conditions with particular materials coacervation takes place, resort may be had to the formation of a ternary diagram from a testing of various amounts of pigskin gelatin and sodium sulphate solution, whereas [illegible] results of testing various amounts of [illegible] with an ammonium sulphate solution. [illegible] of coacervation by use of a salt, the salt attracts water away from the colloid material causing the colloid material to separate or unmix, forming, in the vessel in which this step is taken, after they are allowed to separate by gravity, a colloid-rich fluid in the bottom and a layer extremely poor in colloid material on top. The tests which are made to determine the coacervate region as far as amounts of material are concerned can be done with the colloid sol and the salt solution without the oil. Inasmuch as it is impractical to work with solutions of gelatin in which there is less than 80% water, because of viscosity, the diagrams of Figs. 4 and 5 deal in that portion of the ternary scale above 80% water. The line 20 in Fig. 4 and the line 21 in Fig. 5 represent 30% water, the horizontal lines being indexed with the intermediate percentages of water. Coacervation is noticed by a clouding effect appearing in the sol which transmits less light than normal. This may be noted by passing a beam of light through the sol as the salt solution is added and estimating by eye the change towards a cloudiness, or an electric photometer may be used. A particular sol is made of the pigskin gelatin and various solutions of sodium sulphate in water are added thereto. Referring to Fig. 4, with a starting point of any place on line 23, that is to say any sol of gelatin and water having less than 20% gelatin content, by weight, the aqueous sodium sulphate solution is added. For instance, if a 10% gelatin in water sol is used, the starting point would be 24 (Fig. 4) on line 23. If now a 15% solution of sodium sulphate in water, as would be plotted at point 25, is added slowly which would be plotted along the dotted line 26, at point 27 a clouding effect will be noticed which means that the gelatin in water sol is changing so that the entire mass of gelatin in a liquid phase is contracted because of the increased interaction between the gelatin molecules. This clouding effect, first noticed at point 27, will continue as more of the sodium sulphate solution is added. During the experiments to determine the coacervate line 28 by various experiments with different concentrations of sol and salt solution, the ingredients are kept at about 50° centigrade. As another example in determining the line 28 of Fig. 4, a 17½% sol of gelatin in water, represented by point 29, is treated with a 12½% solution of sodium

(7) In respect to subparagraph (2) of Interrogatory 7(a), "specific parts" of the specification in which Macauley

1958), Paper No. 9 (Amendment filed on or about June 5, 1959)

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sulphate in water as represented by point 30. As this sodium sulphate solution is added to the aqueous gelatin sol, the addition takes the mixture along the line 31 toward point 30, the clouding effect of coacervation becoming apparent at point 32. By making a number of such experimental additions of the sodium sulphate solution to various sol concentrations, the contour of line 28 may be ascertained and the ranges within which coacervation occurs by the addition of sodium sulphate solution to the gelatin sol may be ascertained. The region to the right of line 28 is the coacervate region of the mixture but the addition of salt solution should not be carried far past the line 28 in actual practice, the more salt solution added the more aggregation occurring until a lumpy mass is formed. In a similar manner the line 33 of Fig. 5 may be determined by the use of ammonium sulphate solution.

It will be evident that the ammonium sulphate solution is not as efficient in action as the sodium sulphate solution and the same differences occur with other salts. Useful salts for coacervation may be made from the cations

$$Na > K > Rd > Cs > NH_4 > Li$$

and the anions

$$So_4 > \text{citrate} > \text{tartrate} > \text{acetate} > Cl$$

such being arranged in the order of their effectiveness in this process.

When oil droplets are present the gelatin still in the liquid phase starts to draw together entrapping the oil droplets by deposition of the sol material around them individually as nuclei, forming a strong shell-like wall, and upon gelation of the colloid material the capsules are complete.

Reference has been made to the fact that the size of the pores in the encaspsulated material may be controlled during the gelling process. The faster the gelation of the colloid the finer the pore size of the gelled structure will be, and vice versa. As was said with reference to Fig. 3, the gelation of the gelatin was accomplished by pouring the coacervated mixture, amounting to about a gallon and a half, into 10 gallons of relatively cool water —19° centigrade. This causes rapid cooling and rapid gelation of the gelatin, resulting in a pore size so small that the escapsulated trichlorodiphenyl cannot escape through the capsule walls. Less rapid cooling will result in pores of larger size and the oil used may gradually escape or not as is determined by the size of the pores in the encapsulating film and the size of the oil molecules. That capsules made in accordance with the process of Fig. 3 actually retain the trichlorodiphenyl oil has been proved in various ways. Some of the dried capsular material was placed in a Soxhlet extractor with toluene and subjected to extraction for a week. The material was then removed and dried. Upon crushing the capsular material, oil was released. In another instance paper which had been coated with a film of the capsular material containing 3,3 bis(p-dimethylaminophenyl) 6-dimethylamino phthalide in the oil droplets was similary treated in the Soxhlet extractor. Upon removal and drying, it was used as a transfer sheet by placing it over a paper coated with attapulgite clay. It made marks on the clay-coated sheet when subjected to printing and writing presures, that were as good as those made with an amount of unprotected oil equal to that in the paper. Whereas the unprotected oil evaporated in one day, there was no evidence of any loss of oil from the paper, even though left in the oven for over 90 days at the same temperature.

While the invention, including the ingredients and steps, has been fully outlined in the foregoing specification, the steps are capable of some modification in regard to temperature and amounts of ingredients used, and the ingredients themselves, of course, may be changed, as indicated earlier in the specification.

What is claimed is:

1. The method of making oil-containing microscopic capsules of gellable hydrophilic colloid material, including the steps of making an aqueous sol of a gellable hydrophilic colloid material; emulsifying therein an oil; adding and stirring into the emulsion a previously determined aqueous coacervate salt solution, of such concentration and in such amount as to bring the emulsion into the coacervate region defined by the occurrence of a clouding effect when the aqueous salt solution is added to the colloid solution in the absence of oil, all of the foregoing steps being carried out at a temperature above the gelation point of the colloid material, whereby the colloid material deposits around each oil droplet by coacervate forces, encapsulating each of them; and gelling the colloid material by cooling.

2. The method of claim 1 in which the colloid used is gelatin.

3. The method of claim 1 in which the salt is sodium sulphate.

4. The method of claim 1 in which the colloid material is gelatin and the salt is sodium sulphate.

5. The method of claim 1 in which the salt is ammonium sulphate.

6. The method of claim 1 in which the colloid material is gelatin and the salt ammonium sulphate.

7. The method of claim 1 in which the steps before gelation are carried out above the gelation point of the colloid and the pore size of the capsular material around the oil droplets is made small by the rapid cooling of the coacervate material to cause rapid gelation of the colloid.

8. Oil-containing microscopic capsules made according to the method of claim 1.

9. Oil-containing microscopic capsules made according to the method of claim 2.

10. Oil-containing microscopic capsules made according to the method of claim 3.

11. Oil-containing microscopic capsules made according to the method of claim 4.

12. Oil-containing microscopic capsules made according to the method of claim 5.

13. Oil-containing microscopic capsules made according to the method of claim 6.

14. Oil-containing microscopic capsules made according to the method of claim 7.

References Cited in the file of this patent

UNITED STATES PATENTS

2,183,053	Taylor	Dec. 12, 1939
2,410,110	Taylor	Oct. 29, 1946

FOREIGN PATENTS

454,386	Germany	Jan. 6, 1928
514,047	Great Britain	Oct. 30, 1939

OTHER REFERENCES

Emulsion Technology (1946), pp. 26, 68, 69.

portions of Paper No. 5 (Amendment filed on or about June 11, 1958), Paper No. 9 (Amendment filed on or about June 5, 1959)

IN THE UNITED STATES DISTRICT COURT
FOR THE WESTERN DISTRICT OF NEW YORK

MOORE BUSINESS FORMS, INC., Plaintiff, v. MINNESOTA MINING AND MANUFACTURING COMPANY, Defendant.	)	Civil Action No. CIV. 1972-47

ANSWERS TO PLAINTIFF'S
INTERROGATORIES TO DEFENDANT

Now comes the defendant, Minnesota Mining and Manufacturing Company, by its agent, Waldo G. Bretson, and repeats and answers plaintiff's Interrogatories Nos. 1 through 38, as follows:

Interrogatory No. 1

(a) State the date of incorporation of defendant.

(b) If such date of incorporation is subsequent to January 9, 1962, state the names of all predecessors in interest of defendant and identify them by type of organization (corporation, partnership or sole proprietorship), and date of commencement and termination of existence.

ANSWER:

(a) June 25, 1929.

(b) No answer required.

Interrogatory No. 2

(a) Identify by name, title and business address all officers and directors of defendant from January 9, 1962, to present and state with respect to each such person the exact nature and description of his duties and responsibilities in each such office.

(b) Identify by name, title and business address all officers and directors of predecessors in interest of defendant from January 9, 1962 to present, and state with respect to each such person the exact nature and description of his duties and responsibilities in each such office.

11-13, 16, 17 and 22-29 of the Macauley patent in suit. In respect to defendant's Type 200 carbonless paper which, or the

ANSWER:

(a) Officers of defendant from January 9, 1962 through 1972 include:

William H. Abbott	Vice President, Legal Affairs and General Counsel, 1965-1968
Robert M. Adams	Vice President, Research & Development, 1970-1972
Kelvin T. Bacon	Assistant Treasurer, 1962-1969
Erwin R. Brown	Vice President, Manufacturing, 1971-1972
Richard W. Brust	Vice President, Taxes, 1972
Herbert P. Buetow	President, 1962; Chairman of the Finance Committee, 1963-1967
Archibald G. Bush	Chairman of the Executive Committee, 1962-1965
Edwin H. Church	Assistant Treasurer, 1962-1964
Beverly B. Countryman	Vice President, Purchasing, 1962-1963; Vice President, Purchasing & Traffic, 1964-1967
Bert S. Cross	Executive Vice President, Graphic Products Division, 1962; President, 1963-1965; President and Chairman of the Executive Committee, 1966; Chairman of the Board, Chief Executive Officer and Chairman of the Executive Committee, 1967-1970
Charlton Dietz	Assistant Secretary, 1968-1971; Secretary and Assistant General Counsel, 1972
Joseph C. Duke	Executive Vice President, Sales Administration, 1962
Ralph D. Ebbott	Assistant Treasurer, 1967-1972
Jack J. Erdman	Assistant Treasurer, 1967-1972
Lyle H. Fisher	Vice President, Personnel and Industrial Relations, 1962-1970; Vice President, Public Affairs and Personnel Relations, 1971-1972
Audun R. Fredriksen	Vice President, Europe, 1972
Donald E. Garretson	Assistant Treasurer, 1963-1966; Treasurer, 1967-1971; Vice President and Treasurer, 1972
Leland B. Gehrke	Assistant Treasurer, 1962-1963; Treasurer, 1964-1966; Vice President, International Group, 1972
Donald R. Guthrie	Vice President, Engineering and Manufacturing, 1967-1972

9(b) See documents referred to in answer to Interroga-

Donald O. Hambleton	Assistant Secretary, 1970-1972
Irwin R. Hansen	Treasurer, 1962-1963; Vice President, Finance, 1964-1972
Lloyd A. Hatch	Vice President, Long Range Planning, 1962-1965
Harry Heltzer	Vice President, Reflective Products Division and National Advertising Co., 1962-1963; Vice President, Advertising Services and Protective Products Group, 1964-1966; President, 1967-1969; President and Vice Chairman of the Executive Committee, 1970; Chairman of the Board, Chief Executive Officer and Chairman of the Executive Committee, 1971-1972
Truman J. Henley	Assistant Secretary, 1970-1972
Raymond H. Herzog	Vice President, Duplicating Products and Printing Products Divisions, etc., 1962-1963; Vice President, Graphic Systems Group, 1964-1970; President and Vice Chairman of the Executive Committee, 1971-1972
Robert V. Holton	Vice President, Marketing, 1967-1969
Edward J. Kane	Vice President, Photographic and Printing Products Group, 1971-1972
John G. Kruse	Assistant Secretary, 1962-1963
Carl A. Kuhrmeyer	Vice President, Graphic Systems Group, 1971-1972
Reino O. Laine	Assistant Secretary, 1970-1972
Harold F. Larson	Assistant Treasurer, 1962-1969
Lewis W. Lehr	Vice President, Health Care Products and Services Group, 1972
Carlos W. Luis	Assistant Secretary, 1964-1968; Assistant Secretary and Assistant General Counsel, 1969-1971; Vice President, Federal Government Affairs, 1972
Thomas J. Lyons	Assistant Secretary, 1962-1971; Assistant Secretary and Assistant General Counsel, 1972
Durand W. Maher	Vice President, Marketing, 1972
Cecil C. March	Vice President, Coated Abrasives and Related Products, Adhesives, Coatings and Sealers, and Chemical Divisions, 1962-1966
Roy R. McKenzie	Vice President, Photographic Products Group, 1966-1970

(e) Identify with particularity all documents known to or in possession, custody or control of defendant that constitute, relate or refer to the allegations made by defendant

Complaint are "3M" Brand Carbonless Paper ·rType 100. and "3M"

William L. McKnight	Chairman of the Board and Chief Executive Officer, 1962-1966; Honorary Chairman of the Board, 1967-1972
Robert W. Mueller	Vice President, Tape and Allied Products Group, 1962-1971; Vice President, Health Care Products and Services Group, 1972
William E. Olson	Vice President, Purchasing, 1969-1970; Vice President, Purchasing and Traffic, 1971-1972
Maynard H. Patterson	Vice President, International Group, 1962-1971
Cyril P. Pesek	Vice President, Engineering and Staff Manufacturing, 1962-1965; Vice President, Corporate Long Range Planning and Engineering, 1966-1969
Richard L. Post	Assistant Secretary, 1962-1968; Assistant Secretary and Assistant General Counsel, 1969
Richard S. Priebe	Vice President, Public Affairs, 1969-1970
Willis C. Rech	Assistant Treasurer, 1970-1972
Clarence B. Sampair	Executive Vice President, Tape Products Group and International Division, 1962-1965; Chairman of the Finance Committee, 1968-1970
Walter J. Schmit	Assistant Secretary, 1968-1972
Donald P. Selleck	Vice President and Controller, 1972
Richard L. Sheppard	Vice President, Marketing, 1970-1972
Robert H. Stenberg	Assistant Treasurer, 1967-1972
George W. Swenson	Vice President, Roofing Granules Division, 1962-1966
James A. Thwaits	Vice President, Tape and Allied Products Group, 1972
Hugh J. Tierney	Vice President, Reinforced Plastics Division, 1962-1965
Robert H. Tucker	Secretary, 1962; Vice President, Public Relations and Secretary, 1963-1968; Vice President, Legal Affairs, General Counsel and Secretary, 1969-1971; Vice President, Legal Affairs and General Counsel, 1972
George J. Wachholz	Vice President, Photographic Products Group, 1964-1965
Charles W. Walton	Vice President, Research and Development, 1962-1969
Robert L. Westbee	Vice President, Electrical Products Group, 1962-1972

as set forth in paragraph 10 of defendant's Answer to the

Complaint are "3M" Brand Carbonless Paper ·rType 100. and "3M"

Louis F. Weyand	Vice Chairman of the Executive Committee, 1962
John P. Whitcomb	Vice President, Marketing, 1962; Vice President, Sales Administration, 1963-1965; Vice President, Marketing, 1966; Vice President, Abrasives, Adhesives, Building Services and Chemical Groups, 1967-1972
Robert N. Wolfe	Vice President, Advertising Services and Protective Products Group, 1967-1972
Edgar K. Yucel	Assistant General Counsel, 1970

The business address of each of the foregoing persons during the period or periods during which they are (were) officers is: c/o Minnesota Mining and Manufacturing Company, St. Paul, Minnesota, the exact current address of said company being: 3M Center, St. Paul, Minnesota 55133.

Directors of defendant from January 9, 1962 through 1972 include:

William H. Abbott	1965-1972	3M Center St. Paul, Minnesota 55133
Robert M. Adams	1970-1972	"
Joseph W. Barr	1971-1972	American Security & Trust Co. Suite 301, 15th Street & Pennsylvania Ave. N.W. Washington, D. C. 20013
Herbert P. Buetow	1962-1967	3M Center St. Paul, Minnesota 55133
Archibald G. Bush	1962-1965	Deceased
Vincenzo Cazzaniga	1970-1972	Via Di Porta Latina, 8 00179 Rome, Italy
John L. Connolly	1962-1964	3M Center St. Paul, Minnesota 55133
Bert S. Cross	1962-1972	"
Joseph C. Duke	1962	"
Ralph H. Dwan	1962-1969	Deceased
Leland B. Gehrke	1972	3M Center St. Paul, Minnesota 55133
Donald R. Guthrie	1969-1972	"
Irwin R. Hansen	1968-1972	"

plaintiff learned ever more concerning defendant's Type 100

200 carbonless papers and gave defendant feedback relative to

Harry Heltzer	1965-1972	3M Center St. Paul, Minnesota 55133
Raymond H. Herzog	1965-1972	"
Cecil C. March	1963-1966	"
William L. McKnight	1962-1972	"
Robert W. Mueller	1965-1972	"
John G. Ordway	1962-1965	Deceased
John G. Ordway, Jr.	1972	c/o MacArthur Company 936 Raymond Avenue St. Paul, Minnesota 55114
Richard Ordway	1966-1971	1207 Pioneer Building St. Paul, Minnesota 55101
Maynard H. Patterson	1965-1972	3M Center St. Paul, Minnesota 55133
Cyril P. Pesek	1962-1968	"
Clarence B. Sampair	1962-1970	"
Robert H. Tucker	1972	"
Charles W. Walton	1967-1969	"
Robert L. Westbee	1963-1972	"
Louis F. Weyand	1962	"
John F. Whitcomb	1966-1972	"

(b) No answer required.

Interrogatory No. 3

(a) Identify all persons, whether natural or judicial, who own at least twenty percent (20%) of the outstanding stock of defendant.

(b) Identify all persons, whether natural or judicial, in whom defendant owns an interest of at least twenty percent (20%).

ANSWER:

(a) No answer required.

(b) U. S. Subsidiaries:

American Lava Corporation
Big Rock Stone & Material Corporation
Burgess Cellulose Company
Dynacolor Corporation
Eastern Heights Agency, Inc.
Eastern Heights State Bank of St. Paul

200 carbonless papers and gave defendant feedback relative to

Minnesco Corporation
Minnesota Mining and Manufacturing International Company
Minnesota (3M) Export, Inc.
Minnesota (3M) Inter-America, Inc.
National Advertising Company
National Synthetic Rubber Corporation
Prehler Electrical Insulation Company
Riker Laboratories, Inc.
3M Business Products Sales, Incorporated
Wonewok Lodge, Inc.

Subsidiaries Outside the U.S.:

Laboratorios Riker S.A.
Minnesota (3M) Argentina S.A.C.I.F.I.A.
Minnesota Mining and Manufacturing (Australia) Pty. Limited
Riker Laboratories Australia Pty. Limited
Fobelux S.A.
3M Belgium S.A.-N.V.
Trieme S.A.
3M do Brasil Limitada
Minco Corporation Limited
Minnesota Mining and Manufacturing of Canada Limited
Riker Pharmaceutical Company Limited
Salisbury Cruises Limited
3M Colombia S.A.
3M A/S
Minnesota Mining and Manufacturing Company Limited
Minnesota 3M Laboratories Limited
Minnesota 3M Research Limited
Oy Suomen 3M Company AB
Europeenne de Recherches & d'Applications Pharmacodynamiques S.A. (EURAP)
Groupe Pharmaceutique Riker S.A.
Minnesota "3M" France, S.A.
Photo Cine Stock, S.A.
Photo "3M" France, S.A.
Societe Nouvelle Moser & Cie S.A.
Minnesota Mining and Manufacturing Company mbH
Minnesota 3M Hellas S.A.I.
Minnesota 3M Limited
Minas de Oriente, S.A. (Minorsa)
3M Far East Limited
3M Italia S.p.A.
Marupi-Riker Company, Ltd.
Minnesota (3M) East Africa, Limited
Minnesota (3M) Middle East, S.A.L.
Minnesota (3M) Malaysia Sdn. Berhad
Minnesota (3M) de Mexico, S.A. de C.V.
Riker, S.A. de C.V.
Minnesota "3M" Maroc, S.A.
Societe Civile Immobiliere "Anabou"
Minnesota (Nederland) N.V.
Minnesota (3M) Finance N.V.
Riker Laboratories (N.Z.) Limited
Minnesota Mining and Manufacturing A/S
Minnesota (3M) de Centroamerica S.A.
Minnesota (3M) del Peru S.A.
Minnesota (3M) Philippines, Inc.
Minnesota (3M) de Portugal, Limitada
Minnesota (3M) de Puerto Rico, Inc.
Minnesota (3M) Singapore Private Limited
Minnesota Mining and Manufacturing Company (South Africa) (Proprietary) Limited

10(d) Describe fully the specific activities of plaintiff upon which defendant has allegedly

Riker Laboratories Africa (Proprietary) Limited
Minnesota de Espana, S.A.
Minnesota Mining and Manufacturing AB
Harust A.G.
Minnesota Europe S.A.
Minnesota Mining Products A.C.
3M Taiwan Limited
Minnesota (3M) Thailand Limited
Minnesota (3M) de Venezuela, C.A.

investment in allegedly infringed [illegible] by plaintiff of defendant's great

Interrogatory No. 4

(a) State fully the reasons that are the basis for the allegation in paragraph 7 of the Answer herein that U.S. Patent No. 3,016,308 is invalid for failing to meet one or more of the conditions specified in Section 102 of Title 35, United States Code, reciting such reasons separately with respect to each of paragraphs (a), (b), (c), (d), (e), (f) and (g) of Section 102.

(b) Identify separately all documents known to or in the possession, custody or control of defendant that constitute, relate or refer to the claim of invalidity of said patent under each of paragraphs (a), (b), (c), (d), (e), (f) and (g) of Section 102.

ANSWER:

(a) As presently advised, Macauley Patent No. 3,016,308 in suit is invalid under 35 U.S.C. §102 because, under section (a), before made by Macauley the alleged invention was "known or used by others in this country" and was "patented or described in a printed publication" in this country; under section (b), the alleged invention was "patented or described in a printed publication" in this country "more than one year prior" to August 6, 1957, the date on which Macauley application Serial No. 676,574 upon which the patent in suit issued was filed; under section (e), the alleged invention was "described in a patent granted on an application for patent by another filed in the United States" before Macauley's alleged invention; under section (f), Macauley "did not himself invent the subject matter" which he patented; and under section (g), before Macauley's alleged invention the same had been "made in this country by another who had not abandoned, suppressed, or concealed it". Illustrating the foregoing bases recited under 35 U.S.C. §102, sub-sections (e), (f) and (g) are the following patents:

**Stevens U.S. Patent No. 1,453,859 granted May 1, 1923 on application filed August 7, 1918

**Robinson U.S. Patent No. 2,694,643 granted November 16, 1954 on application filed December 1, 1951

**Green U.S. Patent No. 2,730,456 granted January 10, 1956 on application filed June 30, 1953

*Green U.S. Patent No. 2,800,457 granted July 23, 1957 on application filed June 30, 1953

Schoch U.S. Patent No. 2,876,160 granted March 3, 1959 on application filed July 26, 1954

11(a)(3) Knowledge by plaintiff of defendant's great investment in allegedly infringed [illegible]

Those of the listed patents designated by either a single asterisk (*) or a double asterisk (**) illustrate also the foregoing bases recited under 35 U.S.C. §102(a), with those carrying the double asterisk (**) additionally being applicable under 35 U.S.C. §102(b).

(b) See patents listed in answer to (a) above. Also opinion dated May 11, 1962 re: Patent No. 3,016,308 by attorney Donald M. Sell of Carpenter, Abbott, Coulter & Kinney, attorneys at law and Patent Counsel for defendant, said opinion being transmitted by Mr. Sell's letter dated May 14, 1962 on the letterhead of Carpenter, Abbott, Coulter & Kinney to Mr. W. G. Bretson, Minnesota Mining and Manufacturing Company; and letter dated January 30, 1973 on the letterhead of defendant from Dr. Dean A. Ostlie to Alexander, Sell, Steldt & DeLaHunt, attorneys at law and Patent Counsel for defendant, attention attorney G. L. Griswold.

Interrogatory No. 5

(a) State fully the reasons that are the basis for the allegation in paragraph 7 of the Answer herein that U.S. Patent No. 3,016,308 is invalid for failing to meet one or more of the conditions specified in Section 103 of Title 35, United States Code.

(b) Identify with particularity all documents known to or in the possession, custody or control of defendant that constitute, relate or refer to the claim of invalidity of said patent under Section 103.

ANSWER:

(a) As presently advised, Macauley Patent No. 3,016,308 in suit is invalid under 35 U.S.C. §103 because the subject matter of the alleged invention described and claimed therein "would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains". In addition to the patents referred to in the answer to Interrogatory 4(a), see:

Raab U.S. Patent No. 2,581,441 granted January 8, 1952 on application filed February 6, 1948

Wallenmeyer U.S. Patent No. 2,650,895 granted September 1, 1953 on application filed February 24, 1947

(2) Documents that indicate justifiable reliance

Green U.S. Patent No. 2,712,507 granted July 5, 1955 on application filed June 30, 1953

Green U.S. Patent No. 2,730,457 granted January 10, 1956 on application filed June 30, 1953

Green U.S. Patent No. 2,800,458 granted July 23, 1957 on application filed June 30, 1953.

(b) See patents listed in answer to (a) above. See also answer to Interrogatory 4(b).

Interrogatory No. 6

(a) State fully the reasons that are the basis for the allegation in paragraph 7 of the Answer herein that U.S. Patent No. 3,016,308 is invalid for failing to meet one or more of the conditions specified in Section 101 of Title 35, United States Code.

(b) Identify with particularity all documents known to or in the possession, custody or control of defendant that constitute, relate or refer to the claim of invalidity of said patent under Section 101.

ANSWER:

(a) In respect to 35 U.S.C. §§102, 103 and 112, incorporated by reference in 35 U.S.C. §101, see answers to Interrogatories Nos. 4, 5 and 7. The Macauley patent in suit additionally is invalid as failing to disclose any "useful process" or "manufacture" or "composition of matter or any new and useful improvement thereof", especially in respect to any microscopic discrete rupturable capsules wherein the shell material comprises a chemical condensation polymer (as that term is understood to have been employed in the Macauley patent in suit), or any method for making such a capsule.

(b) See answers to Interrogatories 4(b), 5(b) and 7(b).

Interrogatory No. 7

(a) State fully the reasons upon which defendant basis its allegation contained in paragraph 7 of the Answer herein that U.S. Patent No. 3,016,308 is invalid for failing to meet one or more of the conditions specified in Section 112 of Title 35, United States Code, specifically pointing out and identifying:

(1) By reference to specific parts of specific claims, the manner in which the claims of the patent in suit do not particularly point out or distinctly claim the subject matter which the applicant regards as the invention;

Macauley patent in suit either at this time or at any time

12(c) Identify with particularity all documents known

(2) By reference to specific parts of the specification, the manner in which the written description of the invention does not enable any person skilled in the art to make and use the same;

(3) By reference to specific parts of the application, the basis on which defendant alleges that the specification does not set forth the best mode contemplated by the inventor of carrying out the invention.

(b) Separately with respect to each of subparagraphs (1), (2) and (3) of paragraph (a) of this interrogatory, identify with particularity all documents known to or in the possession, custody or control of defendant that constitute, relate or refer to the claim of invalidity of said patent under Section 112.

ANSWER:

(a) As presently advised, Macauley Patent No. 3,016,308 in suit is invalid under 35 U.S.C. §112 because, in respect to microscopic discrete rupturable capsules wherein the shell material comprises a chemical condensation polymer, the Macauley specification fails to present a written description of the "manner and process of making" such capsules "in such full, clear, concise and exact terms as to enable any person skilled in the art ... to make and use the same" for practical purposes, e.g., in carbonless papers as herein accused. If a mode was known to Macauley by which to operably and usefully make such capsules as of August 6, 1957, the filing date of the application upon which the Macauley patent is based, Macauley failed to disclose it therein, in which event the patent is also invalid as failing to "set forth the best mode contemplated" by Macauley for making such capsules. Further in response -

(1) In respect to sub-paragraph (1) of Interrogatory 7(a), the failure of the Macauley patent to teach the manufacture of microscopic discrete rupturable capsules having shell material comprising a chemical condensation polymer, which capsules are useful and operative in carbonless papers such as here charged to infringe, undermines the validity of each of the claims in suit, particularly in view of plaintiff's position that each of said claims literally encompasses capsules having shell material comprising a chemical condensation polymer.

12(c) Identify with particularity all documents known

(2) In respect to subparagraph (2) of Interrogatory 7(a), "specific parts" of the specification in which Macauley failed to give sufficient teaching include those portions purporting to describe the manufacture of a useful microscopic discrete rupturable capsule having shell material comprising a chemical condensation polymer, especially Example IV, Col. 9, lines 17-45, and Table 2 (particularly as relating to melamine formaldehyde).

(3) In respect to subparagraph (3) of Interrogatory 7(a), and assuming without knowing that Macauley on August 6, 1957 was aware of an operable mode, see portions referred to in paragraph (2) above.

(b) Affidavit of Dean A. Ostlie executed March 2, 1968 and filed in Matson U.S. Application Serial No. 567,723 (maturing on June 23, 1970 as U. S. Patent No. 3,516,941); affidavit of Dean A. Ostlie executed July 13, 1972 and filed in Netherlands Application No. 288,246, filed July 28, 1963 (said application still pending); Meeting report dated September 22, 1965 from Dr. Dean A. Ostlie to Messrs. R. Boldt, W. Bretson and others; and report on encapsulation dated May 10, 1962 to Mr. W. S. Friedlander from R. Gobran.

Interrogatory No. 8

(a) Point out by reference to the file history of U.S. Patent No. 3,016,308 the specific restrictions, if any, that may have occurred by reason of the proceedings had or taken in the United States Patent Office in the prosecution of the application leading to U.S. Patent No. 3,016,308, that allegedly provide the basis for the allegation contained in paragraph 8 of the Answer herein that plaintiff is estopped from maintaining the same in such scope as to cover or embrace any article made, used or sold or process employed by defendant.

(b) Identify with particularlity all documents known to or in the possession, custody or control of defendant that constitute, relate or refer to the claim of estoppel made in paragraph 8 of the Answer herein.

ANSWER:

(a) As presently advised, the estoppel is illustrated by the disclosure of the patent specification coupled with those

portions of Paper No. 5 (Amendment filed on or about June 11, 1958), Paper No. 9 (Amendment filed on or about June 5, 1959) and Paper No. 12 (Amendment filed on or about October 31, 1960), which discuss "free flowing powder" as that term is employed in each of the claims of the Macauley patent in suit, and with that additional portion of said Paper No. 9 which discusses the capsule wall thickness.

(b) The patent in suit and its file wrapper. Also opinion of attorney Sell referred to in answer to Interrogatory No. 4(a).

Interrogatory No. 9

(a) State fully the reasons upon which defendant basis its allegation contained in paragraph 9 of the Answer herein that the claims of U.S. Patent No. 3,016,308 cannot be read on any product manufactured, used or sold by defendant, or on the use of such product and that said claims are therefore not infringed, specifically pointing out and identifying:

(1) By reference to specific parts of specific claims and to specific parts of the disclosure of the patent, the manner in which the claims of the patent in suit are allegedly interpreted to avoid infringement thereof by defendant;

(2) By reference to specific parts of specific claims and to specific prior art patents and publications, the manner in which the claims of the patent in suit are allegedly interpreted to avoid infringement thereof by defendant;

(3) By reference to specific parts of specific claims and to specific parts of the file history of the prosecution before the United States Patent Office of the application from which said Letters Patent issued, the manner in which the claims of the patent in suit are allegedly interpreted to avoid infringement thereof by defendant.

(b) Identify with particularity all documents known to or in the possession, custody or control of defendant that constitute, relate or refer to the allegations made by defendant in paragraph 9 of the Answer herein, including, without limitation the specific prior art patents and publications that have a bearing on the manner in which the claims of U.S. Patent No. 3,016,308 should be interpreted.

ANSWER:

(a)(1) In answer to defendant's Interrogatory No. 1, plaintiff has charged defendant with infringement of claims 8,

11-13, 16, 17 and 22-29 of the Macauley patent in suit. In respect to defendant's Type 200 carbonless paper which, or the production of which, is herein charged to infringe each of said claims (as well as in respect to defendant's Type 100 carbonless paper), and as presently advised -

Claim 8 of the Macauley patent in suit is not infringed because the process by which are produced the microscopic rupturable capsules present therein does not produce "a free flowing powder" of capsules; and said process does not include a "continuous phase of an emulsion" as required in said claim, for example, defendant's microscopic capsules are not produced "by first providing a stable emulsion": cf. Col. 4, lines 35-38 of the patent in suit.

Claim 11 is not infringed because at no stage did the microscopic rupturable capsules exist as a "free flowing powder", and further said capsules do not have an outer shell with "a thickness comprising from about 1/10 to 1/3 of the capsule diameter", but instead have a much lesser thickness in relation to capsule diameter. Since claims 12, 13, 16, 17 and 22-29 are fully dependent upon and thus contain each of the limitations of said claim 11, these claims likewise are not infringed. Claim 26 additionally is not infringed because defendant's carbonless paper does not comprise "a colored transfer substance", and claim 28 is not infringed because defendant's product does not comprise "a colorless dye-former capable of producing a color when in the presence of an acidic substance".

(a)(2) See prior art cited in answer to Interrogatories Nos. 4 and 5, particularly Green Patents Nos. 2,712,507 and 2,800,457.

(a)(3) See answer to Interrogatory 8(a).

9(b) See documents referred to in answer to Interrogatories 9(a)(2) and 9(a)(3) above, and in addition see defendant's South African Patent No. 62/939 granted January 10, 1963, defendant's British Patent No. 989,264 granted January 11, 1966, and Matson U.S. Patent No. 3,516,941 granted June 23, 1970, particularly Example 18 of the latter, which discloses, in detail sufficient to develop the issue here, the process of manufacturing defendant's capsules. In this regard, see also the Ostlie affidavits cited in answer to Interrogatory 7(b). Other documents are letters from Dr. Dean A. Ostlie, dated July 11, 1972 to Kinney, Alexander, Sell, Steldt & DeLaHunt, attention attorney S. G. DeLaHunt, and from Dr. Ostlie dated January 30, 1973 to Alexander, Sell, Steldt & DeLaHunt, attention attorney G. L. Griswold. Other documents such as defendant's confidential commercial manufacturing standards, also, of course, relate to the production of defendant's capsules, but disclosure thereof to plaintiff, which is a competitor of defendant, is unnecessary to development of the infringement issue.

Interrogatory No. 10

(a) Describe fully the products referred to by the defendant in paragraph 10 of the Answer herein which have been manufactured, used and sold throughout the United States by defendant.

(b) Describe fully the processes referred to by the defendant in paragraph 10 of the Answer herein which have been employed by defendant.

(c) State fully, with specificity, the reasons upon which defendant basis its allegation that plaintiff has:

(1) Known of the manufacture, use and sale of infringing products by defendant;

(2) Purchased infringing products from defendant;

(3) Encouraged defendant to market infringing products;

(4) Acquiesced in defendant's infringing activities.

(d) Describe fully the specific activities of plaintiff upon which defendant has allegedly relied as set forth in paragraph 10 of the Answer herein.

(e) Identify with particularity all documents known to or in possession, custody or control of defendant that constitute, relate or refer to the allegations made by defendant in paragraph 10 of the Answer herein, including, without limitation, documents which constitute, relate or refer to each of paragraphs (a), (b), (c) and (d) of this Interrogatory.

ANSWER: [Note: For clarity, the several sub-parts of Interrogatory 10 are repeated at the beginning of the answer specifically directed thereto.]

10(a) Describe fully the products referred to by the defendant in paragraph 10 of the Answer herein which have been manufactured, used and sold throughout the United States by defendant.

Answer: 10(a) "3M Brand Carbonless Paper - Type 100 (Previously branded "ACTION" paper)

"3M Brand Carbonless Paper - Type 200

Documents relating to the production of the Type 100 paper are identified in answer to Interrogatory 9(b) above. Capsules employed in defendant's carbonless paper - Type 200 are substantially the same.

10(b) Describe fully the processes referred to by the defendant in paragraph 10 of the Answer herein which have been employed by defendant.

Answer: 10(b) See answer to Interrogatory 10(a) above.

10(c) State fully, with specificity, the reasons upon which defendant basis its allegation that plaintiff has:

(1) Known of the manufacture, use and sale of infringing products by defendant;

Answer: 10(c)(1) By comparison of sub-parts (c)(1) through (c)(4), inclusive, with paragraph 10 of defendant's Answer to the Complaint upon which the interrogatory is purportedly based, defendant could, with propriety, unqualifiedly answer these sub-parts in the negative for the reason that defendant presents no "allegation" as to "infringing products by defendant", but instead expressly denies any and all infringement by defendant. In the interest of prompt development of the issues, however, defendant will answer this portion of the interrogatory based upon paragraph 10 of defendant's Answer, viz., in reference to products "believed to be complained of by plaintiff".

Products "believed to be complained of by plaintiff"

as set forth in paragraph 10 of defendant's Answer to the Complaint are "3M" Brand Carbonless Paper - Type 100, and "3M" Brand Carbonless Paper - Type 200. Plaintiff has been continuously purchasing defendant's Type 100 carbonless paper since 1962 or early 1963, and plaintiff has been continuously purchasing defendant's Type 200 carbonless paper since about 1968. Plaintiff well knew or should have known of the nature of these products and of their manufacture since the inception of plaintiff's purchases thereof in 1963 and 1968, respectively. Thus -

On February 15, 1963, defendant was sued by National Cash Register Company ("NCR") in the United States District Court for the Northern District of Indiana at Fort Wayne, Civil Action No. 1425. In this action, defendant's Type 100 carbonless paper (then "ACTION" paper) was the product charged as an infringement. The record in the Fort Wayne case discloses the nature and method of making said Type 100 paper and more particularly of the microscopic rupturable capsules therein contained. See particularly the affidavit of Dr. Libby executed October 24, 1963 and filed therein, said affidavit and related documents being available to the public with no protective order imposed thereon by the Indiana Court. Plaintiff herein was well aware of NCR's action against defendant through publicity in the news media. Plaintiff Moore requested, and under date of June 19, 1963 received, an indemnification from defendant in respect to plaintiff Moore's sales in the United States of defendant's Type 100 carbonless paper. Thereafter, in 1963, plaintiff Moore demanded from defendant an indemnification in respect to its purchases of defendant's Type 100 carbonless paper applicable to plaintiff Moore's sales in Canada, and under date of December 20, 1963 received such an indemnification.

During the course of 1963 and thereafter, through publicity by defendant and through direct contacts with defendant,

plaintiff learned ever more concerning defendant's Type 100 carbonless paper and microscopic rupturable capsules constitutin an essential component thereof.

At all times from its initial marketing until 1971, defendant's Type 100 paper was plainly marked with the notice "PATENTS APPLIED FOR". Commencing in the year 1963, defendant's patents containing disclosures in respect to its Type 100 carbonless paper and the microscopic rupturable capsules therein contained were published in foreign countries: see answer to Interrogatory No. 30.

Thus, while much information concerning the general nature of defendant's product was known to plaintiff Moore through its direct contacts with defendant, detailed information, down to the chemistry involved, was publicly available to Moore from sources called to its attention by defendant.

Commencing in 1967 (or 1968), plaintiff learned of defendant's marketing of its Type 200 carbonless paper, and through publicity by defendant and from direct contacts with defendant, plaintiff learned of the nature of the Type 200 product and of the fact in particular that the microscopic rupturable capsules thereof were substantially the same in nature and function as those of the Type 100 paper.

10(c)(2) Purchased infringing products from defendant;

Answer: Plaintiff purchases of Type 100 paper from defendant have increased from about $1,500 in 1963 to about $935,000 in 1971. The sales of Type 200 paper from defendant to plaintiff increased from about $42,000 in 1969 to about $182,000 in 1971.

10(c)(3) Encouraged defendant to market infringing products;

Answer: Plaintiff worked with defendant both at the time of the introduction, respectively, of its Type 100 and Type

200 carbonless papers and gave defendant feedback relative to the utility of such products, nowing full well that defendant was selling and intended to promote sales of such materials to third parties, such as UARCO and Standard Register. For example, at least as early as March 22, 1963, defendant advised personnel of plaintiff of defendant's intention to conduct a test program involving its Type 100 carbonless paper with UARCO and Standard Register and worked closely with plaintiff in connection with such testing program involving these third parties. Plaintiff nonetheless continued to increase its purchases from defendant, thus encouraging defendant to market its Type 100 and Type 200 carbonless papers in increased quantities both to plaintiff and to others.

10(c)(4) Acquiesced in defendant's infringing activites.

Answer: Despite knowing of defendant's efforts and intentions relative to general marketing of its Type 100, and later its Type 200, carbonless papers, and well knowing of defendant's sales of such products to plaintiff's competitors such as UARCO and Standard Register, plaintiff never objected to these activities on the part of defendant. In April 1963, plaintiff's Associate Director of Research, C. E. Bowe., stated in an intra-company letter to R. D. Sutherland, plaintiff Moore's Vice President and Director of Research, in reference to the general commercialization of defendant's Type 100 product to Moore and others:

> "Since 3M will be dealing also with Standard Register and Uarco and one of these companies may wish to move ahead with customer orders, we should define our position in this regard. In line with conversation earlier this week, Sleuth, you may wish to get a ruling on this point now from our legal advisors."

At no time did plaintiff ever raise any objection to the expansion of defendant's business from and after 1963, but instead encouraged the same.

10(d) Describe fully the specific activities of plaintiff upon which defendant has allegedly relied as set forth in paragraph 10 of the Answer herein.

Answer: See answers to parts (c)(1) through (c)(4) of this Interrogatory 10. In addition, personnel of plaintiff, including Robert H. Allen, plaintiff's Manager, Product Planning, Research Division, acknowledged to defendant's personnel in September 1962 and thereafter that plaintiff "had done some work in encapsulation but had never been successful in producing a product of any type that has reached a commercial stage".

10(e) Identify with particularity all documents known to or in possession, custody or control of defendant that constitute, relate or refer to the allegations made by defendant in paragraph 10 of the Answer herein, including, without limitation, documents which constitute, relate or refer to each of paragraphs (a), (b), (c) and (d) of this Interrogatory.

Answer: Documents responsive or pertinent to this Interrogatory are numerous, extending several inches in depth. Other than any of these as to which defendant will claim privilege, or which contain confidential information, plaintiff's counsel may have access and examine the documents on reasonable notice at the offices of defendant's St. Paul counsel. Subject to working out an appropriate form of protective stipulation or order, such documents as are responsive to the interrogatory and which contain confidential or proprietary information will also be voluntarily shown to plaintiff's counsel other than those which involve details of defendant's manufacturing processes, commercial product standards and related documents. As to the latter, defendant will oppose any disclosure to plaintiff, which is its avowed competitor in the area of carbonless papers, for the reason that defendant's published patent disclosures contain detail sufficiently to develop the issue as to infringement.

Interrogatory No. 11

(a) State fully, with particularity, the reasons upon which defendant basis its allegation contained in paragraph 11 of the Answer herein that plaintiff's claims for damages and an injunction are barred by laches, specifically pointing out and identifying the activities of plaintiff which allegedly constitute:

(1) A long delay in bringing this suit without heretofore protesting or accusing defendant of infringement of U.S. Patent No. 3,016,308;

(2) Knowledge by plaintiff of defendant's allegedly infringing activities;

(3) Knowledge by plaintiff of defendant's great investment in allegedly infringing activities.

(b) Identify with particularity all documents known to or in possession, custody or control of defendant that constitute, relate or refer to the allegation that plaintiff's claims for damages and an injunction are barred by laches.

ANSWER: [Note: For clarity, the several sub-parts of Interrogatory No. 11 are repeated at the beginning of the answer specifically directed thereto.]

11(a) State fully, with particularity, the reasons upon which defendant basis its allegation contained in paragraph 11 of the Answer herein that plaintiff's claims for damages and an injunction are barred by laches, specifically pointing out and identifying the activities of plaintiff which allegedly constitute:

(1) A long delay in bringing this suit without heretofore protesting or accusing defendant of infringement of U.S. Patent No. 3,016,308;

Answer: Insofar as defendant is aware, plaintiff has never mentioned its Macauley Patent No. 3,016,308 in suit to defendant or its personnel until this civil action was filed in January 1972. The patent, however, had issued a decade earlier, on January 9, 1962. From shortly following this earlier date, all as detailed in answer to Interrogatory 10 above, defendant had commercialized first its Type 100 carbonless paper and thereafter its Type 200 carbonless paper, by sale not only to plaintiff Moore but (as plaintiff well knew) also to competitors of Moore.

11(a)(2) Knowledge by plaintiff of defendant's allegedly infringing activities;

Answer: See answers to Interrogatory 10, parts (c)(1) and (c)(2) above.

11(a)(3) Knowledge by plaintiff of defendant's great investment in allegedly infringing activities.

Answer: Defendant will be unable to answer this interrogatory in detail until its discovery is concluded. But from the many contacts between personnel of plaintiff and defendant over a period of years commencing in 1962 or 1963, plaintiff was well aware of the manner in which defendant was increasing its production facilities and its advertising in order to promote and market, on an ever-increasing basis, first defendant's Type 100 carbonless paper and thereafter its Type 200 carbonless paper. Plaintiff could not help but be aware of the substantial expenses and investment on the part of defendant.

11(b) Identify with particularity all documents known to or in possession, custody or control of defendant that constitute, relate or refer to the allegation that plaintiff's claims for damages and an injunction are barred by laches.

Answer: Insofar as applicable to documents which are responsive or pertinent to this Interrogatory, see answer to Interrogatory 10(e).

Interrogatory No. 12

(a) State fully, with particularity, the reasons upon which defendant basis its allegations contained in paragraph 12 of the Answer herein that plaintiff is estopped from in any way enforcing U.S. Patent No. 3,016,308 against defendant, specifically pointing out and identifying:

(1) The activities of plaintiff which allegedly constitute acquiescence by plaintiff in allegedly infringing activities of defendant which were carried on at great and ever increasing expense;

(2) The activities of defendant that constituted justifiable reliance that plaintiff had acquiesced and was acquiescing in infringing activities of defendant.

(b) State fully with particularity whether or not defendant is performing any acts that might constitute invasion of any other property rights of plaintiff on the basis of acquiescence by plaintiff in such acts and reliance thereon by defendant.

(c) Identify with particularity all documents known to or in the possession, custody or control of defendant that constitute, relate or refer to the allegation set forth in paragraph 12 of the Answer herein that plaintiff is estopped from enforcing U.S. Patent No. 3,016,308 including, without limitation:

(1) Documents that indicate acquiescence or lack thereof by plaintiff in acts of defendant;

(2) Documents that indicate justifiable reliance or lack thereof by defendant on plaintiff's alleged acquiescence in acts of defendant.

ANSWER: [Note: For clarity, the several sub-parts of Interrogatory No. 12 are repeated at the beginning of the answer specifically directed thereto.]

12(a) State fully, with particularlity, the reasons upon which defendant basis its allegation contained in paragraph 12 of the Answer herein that plaintiff is estopped from in any way enforcing U.S. Patent No. 3,016,308 against defendant, specifically pointing out and identifying:

(1) The activities of plaintiff which allegedly constitute acquiescence by plaintiff in allegedly infringing activities of defendant which were carried out at great and ever increasing expense;

Answer: As pointed out in the answer to Interrogatories Nos. 10 and 11, there were continual contacts between defendant and plaintiff relative to the marketing by defendant of first Type 100 carbonless paper and later Type 200 carbonless paper not only to plaintiff Moore but to others on an ever-increasing scale. Never did plaintiff object to these activities by defendant or suggest in any way that the Macauley Patent No. 3,016,308 in suit was or might be infringed. Plaintiff's manager of Product Development, Mr. R. H. Allen, in or about September 1962, admitted that plaintiff Moore had no commercial product of its own manufacture containing or based upon microscopic rupturable capsules, although the Macauley patent had then only freshly issued. Moreover, the patentee Macauley himself, in April 1963, apparently was in contact with defendant involving carbonless paper products. Mentioned to defendant's personnel on the occasion was another product concept allegedly developed by Macauley and said to be covered by a patent which had issued in February of 1963. In or about the same time, plaintiff's Central Research Division was studying defendant's Type 100 carbonless paper (then branded "ACTION" paper). While thus being patent conscious and interested in defendant's product, neither Macauley nor any other personnel of plaintiff raised any objection or question in respect to the

Macauley patent in suit either at this time or at any time thereafter until nearly a decade later, when the instant civil action was filed in January, 1972.

12(a)(2) The activities of defendant that constitute justifiable reliance that plaintiff had acquiesced and was acquiescing in infringing activities of defendant.

Answer: Beginning in October 1962, a fund for the accrual of monies from the sales of defendant's Type 100 carbonless paper was set up for the purpose of paying plaintiff back royalties or damages in the unlikely event, should litigation ensue involving the Macauley patent here in suit, that defendant would be held liable. Funds continually accrued through the years 1963, 1964 and part of the year 1965. No action having been taken by plaintiff Moore, the accruals were discontinued in 1965. In 1967 the fund was returned to the Paper Products Division of defendant.

During the period from 1962 through 1971, defendant's advertising and merchandising expenses increased from about $5,000 in 1962 to about $250,000 in the year 1971, such expense aggregating nearly $2 million over the entire period. Defendant capital investment over the same period in facilities for producing first its Type 100 and later its Type 200 carbonless pape was from about $600,000 in 1962 to about $14 million by 1972.

Had defendant known that plaintiff was going to asser the Macauley Patent No. 3,016,308 in suit against its carbonles papers, defendant would not have discontinued the accrual of funds which had theretofore been set up in view of the Macauley patent, would not have disbursed the funds which had accrued, and would not have expended the large amounts in advertising an capital investment without reconciling the problem.

12(b) State fully with particularity whether or not defendant is performing any acts which might constitute invasio of any other property rights of plaintiff on the basis of acqui cence by plaintiff in such acts and reliance thereon by defenda

Answer: This Interrogatory is objected to.

12(c) Identify with particularity all documents known to or in the possession, custody or control of defendant that constitute, relate or refer to the allegation set forth in paragraph 12 of the Answer herein that plaintiff is estopped from enforcing U.S. Patent No. 3,016,308 including, without limitation:

(1) Documents that indicate acquiescence or lack thereof by plaintiff in acts of defendant;

(2) Documents that indicate justifiable reliance or lack thereof by defendant on plaintiff's alleged acquiescence in acts of defendant.

Answer: Insofar as applicable to documents which are responsive or pertinent to this Interrogatory, see answer to Interrogatory 10(e).

Interrogatory No. 13

(a) State fully with particularity the reasons upon which defendant basis its allegation contained in paragraph 13 of the Answer herein, that plaintiff by its conduct has allegedly given defendant an implied license under U.S. Patent No. 3,016,308, specifically pointing out and identifying the [illegible]se acts of plaintiff that constitute such conduct and the consideration flowing from defendant to plaintiff to support such license.

(b) Identify with particularity all documents known to or in the possession, custody or control of defendant that constitute, relate or refer to such an implied license.

ANSWER:

(a) As presently advised, in respect to sales from defendant to plaintiff, the implied license extends from the fact of the sales themselves. In respect to sales by defendant to third parties, as pointed out in answer to Interrogatories 10 and 11, plaintiff was well aware of and encouraged defendant not only to market its carbonless papers to third parties but to increase those sales, all without remuneration to plaintiff. These acts impliedly occurred with plaintiff's consent because of plaintiff's failure at any time to assert that defendant did not have the free right under plaintiff's patents to so conduct itself.

(b) Insofar as applicable to documents which are responsive or pertinent to this Interrogatory, see answer to Interrogatory 10(e).

Interrogatory No. 14

(a) State whether defendant has ever (1) manufactured, (2) had manufactured for it, (3) used, or (4) sold a product which constitutes, comprises, incorporates or includes in any manner microscopic discrete rupturable capsules as defined in Preamble B hereto.

(b) (1) If the answer to Interrogatory No. 14(a) is other than an unqualified negative, identify all such products by trade designation, catalog number or the like;

(2) State the dates of first manufacture, use and sale by defendant of each said product;

(3) State whether such manufacture, use and sale are presently continuing and if not;

(4) Give the dates of termination thereof.

(c) Identify all documents known to or in the possession, custody or control of defendant constituting, referring or relating to each said product.

ANSWER:

(a) Yes.

(b)(1) and (b)(2) Products constituting or including rupturable microscopic capsules commercialized by defendant, together with the year of first manufacture and sale, include:

Product	First Manufacture and Sale
"3M" Brand Carbonless Paper - Type 100 (Marketed as "ACTION" Brand Carbonless Paper from 1962 until about 1967)	1962
"3M" Brand Carbonless Paper - Type 200	1967
"MICROFRAGRANCE" Brand Encapsulated Fragrances	1965
"SCOTCHCAST" Brand Termination Resin, No. 14	1962
"3M" Brand Spot Remover Pads	1964
"3M" Brand Microcapsules	1971
"SAFEGUARD" 123 (inner seal)	1964
"SCOTCH-GRIP" Fastener Adhesive (2353)	1968

(b)(3) and (b)(4) All are continuing products except for the Spot Remover Pads and "SAFEGUARD" 123, which were discontinued in the years 1965 and 1966, respectively.

(c) Objected to.

including microscopic discrete rupturable capsules or processes for making such products.

Interrogatory No. 15

(a) State whether defendant employs persons to design, modify, improve or originate products constituting, comprising, incorporating or including microscopic discrete rupturable capsules or processes for making such products.

(b) If the answer to Interrogatory No. 15(a) is other than an unqualified negative, state the number of persons who are now so employed, identify each person who functions in a managerial capacity with respect to said employed persons, and state the exact nature and description of the duties and responsibilities of each such manager.

(c) Identify all persons who have functioned in a managerial capacity with respect to such employed persons since January 9, 1962, and state the exact nature of the duties and responsibilities of each such manager.

ANSWER:

(a) If this interrogatory is intended to comprehend persons who perform such acts in defendant's employ, whether or not hired to do so, the answer is yes.

(b) The General Manager of the Paper Products Division of defendant, which division has the responsibility for the manufacture and marketing of defendant's Type 200 carbonless paper herein charged to infringe the patent in suit, as well as defendant's Type 100 carbonless paper, is, and has been since its inception, Waldo G. Bretson. The Technical Director of said division, who reports to Mr. Bretson, is, and since 1969 has been, Dr. Buck Stricklin. Each of these persons acts in a managerial capacity with respect to persons in said division performing such acts. The Research Manager of said Paper Products Division is Dr. Dean A. Ostlie.

(c) From January 9, 1962 until Dr. Stricklin replaced him, the Technical Director of the Paper Products Division of defendant was Mr. Alva N. Frye.

Except as here answered, Interrogatory 15 is objected to.

Interrogatory No. 16

(a) State whether defendant employs persons to conduct development with respect to products constituting, comprising, incorporating or including microscopic discrete rupturable capsules or processes for making such products.

(b) If the answer to Interrogatory No. 16(a) is other than an unqualified negative, state the number of persons who are now so employed, identify each person who functions in a managerial capacity with respect to said employed persons and state the exact nature of the duties and responsibilities of each such manager.

(c) Identify all persons who have functioned in a managerial capacity with respect to such employed persons since January 9, 1962, and state the exact nature of the duties and responsibilities of each such manager.

ANSWER:

(a), (b) and (c) See answer to Interrogatory 15.

Interrogatory No. 17

(a) State whether defendant employs persons to manufacture products constituting, comprising, incorporating or including microscopic discrete rupturable capsules.

(b) If the answer to Interrogatory No. 17(a) is other than an unqualified negative, state the number of persons who are now so employed, identify each person who functions in a managerial capacity with respect to said employed persons and state the exact nature of the duties and responsibilities of each such manager.

ANSWER:

(a) See answer to Interrogatory 15(a).

(b) Insofar as "manufacture" relates other than to commercial manufacture, see answer to Interrogatory 15. Insofar as "manufacture" relates to commercial manufacture, the Manufacturing Manager of the Paper Products Division of defendant is Mr. R. C. Bertelsen.

(c) Prior to Mr. Bertelsen, the Manufacturing Managers since January 9, 1962 were R. M. Elias, John E. Spalding and R. J. Baken.

Except as here answered, Interrogatory 17 is objected to.

Interrogatory No. 18

(a) State whether defendant employs persons to solicit sales of products constituting, comprising, incorporating or including microscopic discrete rupturable capsules.

(b) If the answer to Interrogatory No. 18(a) is other than an unqualified negative, state the number of persons who are now so employed, identify each person who functions in a managerial capacity with respect to said employed persons and state the exact nature of the duties and responsibilities of each such manager.

(c) Identify all persons who have functioned in a managerial capacity with respect to such employed persons since January 9, 1962, and state the exact nature of the duties and responsibilities of each such manager.

ANSWER:

(a) See answer to Interrogatory 15(a).

(b) The General Sales Manager of the Paper Products Division of defendant presently is Norman H. Gunderson, who reports to W. G. Bretson.

(c) Prior to Mr. Gunderson and since January 9, 1962, Mr. C. Kraning was General Sales Manager of the Paper Products Division, reporting to Mr. Bretson.

Except as here answered, Interrogatory 18 is objected to.

Interrogatory No. 19

(a) State whether defendant employs persons to prepare or conduct advertising and/or sales promotional material and campaigns with respect to products constituting, comprising, incorporating or including microscopic discrete rupturable capsules.

(b) If the answer to Interrogatory No. 19(a) is other than an unqualified negative, state the number of persons who are now so employed, identify by name, title and address each person who functions in a managerial capacity with respect to said employed persons and state the exact nature of the duties and responsibilities of each such manager.

(c) Identify all persons who have functioned in a managerial capacity with respect to such employed persons since January 9, 1962, and state the exact nature of the duties and responsibilities of each such manager.

ANSWER:

(a) See answer to Interrogatory 15(a).

(b) The Merchandising and Advertising Manager of the Paper Products Division of defendant is Mr. E. F. Anglo.

(c) Prior to Mr. Anglo, and since January 9, 1962, the function of Merchandising and Advertising Manager was filled, in turn, by D. A. Olson, D. K. Huebner, S. A. Lindell, P. G. Montgomery and G. I. Schroepfer.

Except as here answered, Interrogatory 19 is objected to.

Interrogatory No. 20

(a) State when, where and under what circumstances defendant first learned of the manufacture or sale by plaintiff of products constituting, comprising, incorporating or including microscopic discrete rupturable capsules which are identical to or substantially the same as any product illustrated or described in U.S. Patent No. 3,016,308. Kindly include in this answer the names, addresses and titles of defendant's employees who first learned of said products constituting, comprising, incorporating or including microscopic discrete rupturable capsules and the dates on which they so learned.

(b) Identify with particularity all documents constituting, referring or relating to the acquisition of knowledge by defendant of plaintiff's products constituting, comprising, incorporating or including microscopic discrete rupturable capsules, and the present custodian thereof.

ANSWER:

(a) and (b) Defendant does not know of it even to this date, and leaves plaintiff to its proof thereon. Defendant first learned of plaintiff's assertion that plaintiff has manufactured commercial products under the Macauley patent in suit through plaintiff's answer, executed on or about June 14, 1972, to defendant's Interrogatory No. 23.

Interrogatory No. 21

(a) State whether defendant has ever acquired a physical embodiment of any product constituting, comprising, incorporating or including microscopic discrete rupturable capsules manufactured or sold by plaintiff, which product was identical to or substantially the same as any product illustrated or described in U.S. Patent No. 3,016,308.

(b) If the answer to Interrogatory No. 21(a) is other than an unqualified negative, identify (1) the employees who acquired it; (2) the employees who ordered or obtained it; (3) the person or organization from which it was ordered or obtained, and (4) the dates on which it was ordered, and received or obtained.

(c) Identify with particularity all documents which constitute, relate or refer to said acquisition, specifically including but not limited to payment vouchers, statements, purchase orders, invoices and cancelled checks which evidence payments for said product.

ANSWER:

(a) Not to plaintiff's knowledge.

(b) No answer required.

(c) No answer required.

Interrogatory No. 22

(a) Identify the officers, directors and/or employees of defendant who participated in or who were responsible for defendant's decision to market the first-marketed product identified in answer to Interrogatory No. 14 hereinbefore.

(b) State the date on which defendant reached the decision to market said first-marketed product and identify all documents relating, referring to or constituting said decisions, and the present custodian thereof.

ANSWER:

(a) The decision was made by Mr. W. G. Bretson, the General Manager of the division having responsibility for such marketing. Higher management personnel of defendant who knew of such decision were in a position to veto the same but did not.

(b) Late 1961 or early 1962.

Interrogatory No. 23

Identify the officers, directors and/or employees of defendant at the times defendant made its decision to market the products recited in Interrogatory No. 22 hereinbefore, who were aware of manufacture by plaintiff of a product identical to or substantially the same as that illustrated or described in any embodiment of U.S. Patent No. 3,016,308.

ANSWER:

No one, because it is not the fact.

Interrogatory No. 24

(a) Before its first manufacture and/or sale of a product identified in answer to Interrogatory No. 14 hereinbefore, did defendant conduct or have conducted for it an investigation to ascertain the commercial market for such a product?

(b) If the answer to Interrogatory No. 24(a) is other than an unqualified negative, state the results of such investigation, the names and addresses of the persons or organizations which carried out such investigation, and whether the results of such investigation were set forth in one or more written documents.

(c) If such results were set forth in written documents, identify each such document, and all documents relating or referring to such investigation, and the present custodian thereof.

ANSWER:

(a) Yes.

(b) A study of the business forms industry was made by Mr. J. W. Donnelly, Market Service Department, Graphic Products Group of defendant. The investigation resulted in a written

report dated April 7, 1961. Another segmented informal marketing study, made by C. T. Vangsness in summer 1961, in hopes of defining a need for carbonless paper in small roll form for office machines, demonstrated such need.

(c) No documents have been found other than the aforesaid report of April 7, 1961.

Interrogatory No. 25

(a) State whether defendant has at any time entered into agreements or understandings with other manufacturers, prospective manufacturers or users of products constituting, incorporating, comprising or including microscopic discrete rupturable capsules relating to (1) exchange of information, or (2) the furnishing of assistance between the parties with respect to the patent in suit, for the purpose of defending against or invalidating said patent.

(b) If the answer to Interrogatory No. 25(a) is other than an unqualified negative, state (1) the names of the manufacturers with whom agreements or understandings were entered into, (2) the dates thereof, (3) the persons representing defendant, and (4) the persons representing said manufacturers.

(c) Identify all documents constituting, relating or referring to said agreements or understandings, and the present custodian thereof.

ANSWER:

(a) No.

(b) No answer required.

(c) No answer required.

Interrogatory No. 26

(a) State whether defendant ever discussed the patent in suit with any manufacturer, prospective manufacturer or user of products constituting, incorporating, comprising or including microscopic discrete rupturable capsules.

(b) If the answer to Interrogatory No. 26(a) is other than an unqualified negative, state (1) the names of the manufacturers with whom the discussions took place, (2) the dates thereof, (3) the persons representing defendant, and (4) the persons representing such manufacturers at the discussions.

(c) Identify all documents constituting, relating or referring to such discussions, and the present custodian thereof.

ANSWER:

(a) Excluding plaintiff it is believed not.

(b) No answer required.

(c) No answer required.

Interrogatory No. 27

(a) State whether defendant has ever entered into any agreement, or reached any understanding, or discussed with any other manufacturer, prospective manufacturer or user of products constituting, incorporating, comprising or including microscopic discrete rupturable capsules (1) the negotiating with plaintiff with respect to the patent in suit, or (2) the taking of a license under the patent in suit, or (3) being the beneficiary under a covenant not to sue with respect to the patent in suit.

(b) If the answer to Interrogatory No. 27(a) is other than an unqualified negative, state (1) the names of the manufacturers with whom defendant agreed or reached an understanding or had discussions, (2) the persons who represented said manufacturers and defendant, and (3) the dates of said agreements or understandings or discussions.

(c) Identify all documents constituting, relating or referring to such agreements as understandings or discussions, and the present custodian thereof.

ANSWER:

(a) No.

(b) No answer required.

(c) No answer required.

Interrogatory No. 28

(a) Identify any trade associations or like organizations to which defendant has belonged since August 6, 1956, and state whether plaintiff's U.S. Patent No. 3,016,308 or any product of plaintiff which constitutes, comprises, incorporates or includes microscopic discrete rupturable capsules was discussed at any meetings of such trade associations or like organizations subsequent to August 6, 1956.

ANSWER:

(a) Defendant does not understand this interrogatory. If it is intended to inquire whether defendant's agents or employees have discussed either the patent in suit or any product of the type described which originated with plaintiff at any meeting of a trade association or like organization, the answer is no. Whether either of such subjects has been discussed by others, for example, by employees of plaintiff, defendant does not know.

Interrogatory No. 29

(a) Has defendant informed any other manufacturers, prospective manufacturers or users of products constituting, comprising, incorporating or including microscopic discrete rupturable capsules of its belief that any of the claims of the patent in suit are invalid?

(b) If the answer to Interrogatory No. 29(a) is other than an unqualified negative, state the names and addresses of those who were so informed.

(c) Identify all documents constituting, relating or referring to such informing, and the present custodian thereof.

ANSWER:

(a) Insofar as defendant is aware, no statements have been made to such parties at all concerning the patent in suit. Should the occasion arise, defendant will inform the parties of its belief that the patent in suit is invalid.

(b) No answer required.

(c) No answer required.

Interrogatory No. 30

(a) Identify all patents disclosing and/or claiming products constituting, comprising, incorporating or including microscopic discrete rupturable capsules or processes for making such products, owned by defendant or in which defendant has any rights or under which defendant manufactures, uses or sells such products, stating (1) defendant's rights in said patents, (2) the numbers of said patents, and (3) whether the patentees named thereon were employees of defendant at the time of their alleged inventions.

(b) Identify all pending and abandoned patent applications disclosing and/or claiming products constituting, comprising, incorporating or including microscopic discrete rupturable capsules or processes for making such products, owned by defendant or in which defendant has any rights or under which defendant manufactures, uses or sells products constituting, comprising, incorporating or including microscopic discrete rupturable capsules setting forth (1) defendant's rights in said applications, (2) the serial numbers and filing dates of said applications, (3) the names of the alleged inventors of the subject matter claimed in said applications, (4) the location of copies of said applications other than at the U.S. Patent Office, and (5) the present custodian thereof.

ANSWER:

(a) In view of the pertinence of their disclosure as relating to the manufacture and composition of rupturable microscopic capsules in defendant's Type 200 carbonless paper herein

accused as an infringement of plaintiff's patent in suit, as well as defendant's Type 100 carbonless paper, defendant lists the following patents issued to or owned by it:

Ostlie U.S. Patent No. 3,481,759 granted December 2, 1969

Matson U.S. Patent No. 3,516,846 granted June 23, 1970

Matson U.S. Patent No. 3,516,941 granted June 23, 1970

Argentina - Patent No. 139,154 granted May 26, 1964
Argentina - Patent No. 161,076 granted May 30, 1968
Argentina - Patent No. 167,239 granted May 26, 1969

Australia - Patent No. 271,842 granted May 16, 1967
Australia - Patent No. 280,494 granted July 19, 1968
Australia - Patent No. 413,471 granted April 17, 1972

Austria - Patent No. 240,830 granted March 15, 1965
Austria - Patent No. 247,881 granted March 15, 1966
Belgium - Patent No. 615,040 granted September 13, 1962
Belgium - Patent No. 627,711 granted July 29, 1963
Canada - Patent No. 742,643 granted September 13, 1966
Canada - Patent No. 780,358 granted March 12, 1968
Canada - Patent No. 813,846 granted May 27, 1969

Colombia - Patent No. 12,302 granted August 14, 1963
Colombia - Patent No. 12,403 granted August 30, 1963
Denmark - Patent No. 117,413 granted September 21, 1970
Denmark - Patent No. 116,703 granted June 29, 1970
Finland - Patent No. 40,662 granted April 10, 1969
Finland - Patent No. 43,951 granted July 12, 1971
France - Patent No. 1,323,043 granted January 29, 1963
France - Patent No. 1,359,702 granted March 23, 1964
France - Patent No. 1,534,465 granted June 17, 1968

Germany - Patent No. 1,444,414 granted April 10, 1969
Great Britain - Patent No. 1,042,599 granted January 31, 1967
Great Britain - Patent No. 989,264 granted January 11, 1966
Great Britain - Patent No. 1,042,596 granted January 31, 1967
Great Britain - Patent No. 1,207,836 granted April 22, 1971

Holland - Patent No. 134,885 granted August 18, 1972

India - Patent No. 81,124 granted January 18, 1964
India - Patent No. 86,281 granted April 2, 1965
Italy - Patent No. 663,695 granted May 13, 1964
Italy - Patent No. 757,102 granted April 15, 1967
Italy - Patent No. 812,937 granted May 15, 1968

Japan - Patent No. 646,142 granted May 30, 1972

Japan - Patent No. 582,048 granted August 28, 1970

Mexico - Patent No. 85,996 granted November 21, 1967
Mexico - Patent No. 79,388 granted March 31, 1967
Mexico - Patent No. 96,849 granted July 18, 1969

New Zealand - Patent No. 134,017 granted November 11, 1966
Norway - Patent No. 120,965 granted April 15, 1971

Norway - Patent No. 109,622 granted August 20, 1966

South Africa - Patent No. 62/939 granted January 10, 1963
South Africa - Patent No. 63/230 granted November 6, 1963
South Africa - Patent No. 67/4995 granted March 5, 1969

Spain - Patent No. 275,391 granted September 7, 1962
Spain - Patent No. 284,589 granted April 30, 1963
Spain - Patent No. 279,705 granted November 13, 1962

Sweden - Patent No. 301,134 granted October 10, 1968
Sweden - Patent No. 208,985 granted June 23, 1966
Sweden - Patent No. 316,978 granted February 12, 1970

Switzerland - Patent No. 457,368 granted June 15, 1968
Switzerland - Patent No. 411,561 granted April 15, 1966
Switzerland - Patent No. 463,264 granted September 30, 1968

(b) Certain applications now standing abandoned, copies of which are in the custody of defendant's counsel, are identified in the U.S. patents listed in part (a) to this interrogatory, as follows:

U.S. Application Serial No. 175,394 filed February 26, 1962

U.S. Application Serial No. 95,417 filed March 13, 1961

Except as here answered, Interrogatory 30 is objected to.

Interrogatory No. 31

(a) State the date on which defendant first became aware of U.S. Patent No. 3,016,308.

(b) Name the officer, director or employee of defendant who first became so aware and describe the fact situation that made him aware.

(c) Identify all documents constituting, relating or referring to such awareness, and the present custodian thereof.

ANSWER:

(a) About March of 1962, it is believed.

(b) Apparently Gale W. Matson; the fact situation is not known at this date.

(c) 3M Laboratory Notebook #11913, page 46, dated March 2, 1962, issued to Gale W. Matson.

Interrogatory No. 32

(a) State whether any employee, agent or attorney of defendant ever prepared an opinion, oral or in writing, relating to the validity of the patent in suit or the possible infringement thereof by defendant.

(b) If the answer to Interrogatory No. 32(a) is other than an unqualified negative, identify fully each such opinion and state whether its author is a member of the Bar of any country or state or the District of Columbia and under what relationship to defendant he acted in preparing such opinion.

(c) Identify all documents relating or referring to said opinions, and the present custodian thereof.

ANSWER:

(a) Yes.

(b) Letter dated May 14, 1962 on the letterhead of Carpenter, Abbott, Coulter & Kinney, attorneys at law and Patent Counsel for defendant, from attorney Donald M. Sell to W. G. Bretson, then General Manager of the Paper Products Division of defendant, said letter transmitting therewith an opinion re Patent No. 3,016,308 by attorney Sell dated May 11, 1962. Letter dated October 30, 1962 from attorney Sell on the letterhead of Carpenter, Abbott, Coulter & Kinney to Mr. A. L. Frye, then Technical Director of the Paper Products Division of de. ndant. Intra-firm memorandum on the letterhead of Carpenter, Abbott, Coulter & Kinney from attorney William H. Abbott to attorney Sell dated May 21, 1962.

(c) These documents are in the custody of defendant's counsel.

Interrogatory No. 33

(a) State whether defendant has ever marketed any product identified in answer to Interrogatory No. 14 hereinbefore, bearing the number of any United States or foreign patent, or with the notation, Patent Pending, or its equivalent.

(b) If the answer to Interrogatory No. 33(a) is other than an unqualified negative, identify such patent numbers and notations and the product on which each was used.

ANSWER:

(a) Yes.

(b)

"3M" Brand Carbonless Paper - Type 100 (previously "ACTION" Brand Carbonless Paper)

Up to 1971, the notice read:

"PATENTS APPLIED FOR"

From 1971 to date, the notice has read:

"U. S. PATENTS NOS. 3,516,846 3,516,941 OTHERS PENDING"

"3M" Brand Carbonless Paper - Type 200

From the inception of the product until 1971, the notice read:

"PATENTS/APPLIED FOR"

From 1971 to date, the notice has read:

"U.S. Patent Nos. 3481759, 3516846, 3516941"

"SCOTCHCAST" Brand Termination Resin, No. 14

From the inception of the product, the notice has read:

"Patented under one or more of the following patents: U.S. Nos. 2756875, 2932385; Australia Patent No. 223026/57; Canada Patented 1960."

"3M" Brand Spot Remover Pads

From the inception of the product until 1965, the notice read:

"PATENT PENDING"

"SCOTCH-GRIP" Fastener Adhesive (2353)

U.S. Patent No. 3,642,937 and U.S. Patent No. 3,179,143

Interrogatory No. 34

(a) Identify with particularity all catalogs, brochures, advertisements and sales promotional materials utilized by defendant since August 6, 1956, in connection with the use or sale of its products constituting, comprising, incorporating or including microscopic discrete rupturable capsules.

ANSWER:

(a) The bulk of the material sought to be identified in this interrogatory makes specific identification impractical. On reasonable notice defendant will voluntarily produce the material called for at the offices of its St. Paul counsel.

Interrogatory No. 35

(a) Identify all documents, including but not limited to correspondence and memoranda, both to and from other parties and within the organization of defendant, relating or referring to the present action or the charge of infringement made by plaintiff against defendant with respect to the patent in suit.

ANSWER:

(a) Excluding documents and memoranda to, from or by defendant's counsel:

Letter dated June 30, 1972 from J. R. McClintick to R. H. Herzog

Letter dated July 7, 1972 from W. G. Bretson to R. H. Herzog and C. A. Kuhrmeyer

Letter dated July 18, 1972 from R. C. Bertelsen to W. G. Bretson

Letter dated August 9, 1972 from Secretary to R. H. Herzog to David W. Barr

Letter dated September 20, 1972 from D. W. Barr to R. H. Herzog

Letter dated October 18, 1972 from D. W. Barr to R. H. Herzog

Letter dated December 1, 1972 from D. W. Barr to R. H. Herzog

Interrogatory No. 36

(a) State whether defendant has knowledge of any tests performed by defendant, an agent thereof, or a third party, in which the subject of said tests has been a product identified in answer to Interrogatory No. 14 hereinbefore or any precursor or component thereof.

(b) If the answer to Interrogatory No. 36(a) is other than an unqualified negative, describe such tests in detail and identify all documents that constitute the results thereof.

(c) Identify all documents relating or referring to the tests described in answer to Interrogatory No. 36(b), and the present custodian thereof.

ANSWER:

(a) - (c), inclusive. This Interrogatory is objected to.

Interrogatory No. 37

(a) Identify all documents not heretofore identified that are known to or in the possession of defendant referring or relating to products constituting, comprising, incorporating or

all buildings that comprise the facility, and particularly that

including microscopic discrete rupturable capsules or processes for making such products.

(1) Marketed or used by defendant.

(2) Marketed or used by third parties.

ANSWER:

(a) This Interrogatory is objected to.

Interrogatory No. 38

(a) State whether defendant is the owner of U.S. Patent No. 3,516,941.

(b) State whether defendant has ever manufactured, had manufactured for it, used or sold any of the products which constitute, incorporate, comprise or include microscopic discrete rupturable capsules or processes for making the same disclosed in U.S. Patent No. 3,516,941.

(c) If the answer to Interrogatory 38(b) is other than an unqualified negative, identify and describe fully each such products and process, including:

(1) Trade designation, catalog number or the like;

(2) The date of first manufacture, use or sale by defendant of each such product;

(3) Whether such manufacture, use or sale is presently continuing, and if not;

(4) The dates of termination thereof.

(d) Identify all documents known to or in the possession, custody or control of defendant constituting, referring or relating to each such product or process.

ANSWER:

(a) Yes.

(b) Yes.

(c)(1) - (4). See answer to Interrogatory No. 14(b).

(d) Objected to.

Waldo G. Bretson

Waldo G. Bretson

STATE OF MINNESOTA)
) ss.
COUNTY OF RAMSEY)

The said WALDO G. BRETSON, known to me, did appear before me this 16th day of February, 1973, and swore to the above responses being correct to the best of his knowledge and belief.

Notary Public

(3) A complete description of the structure of all buildings that comprise the facility, and particularly that

PLEASE TAKE NOTICE that a

of which the within is a copy, was duly entered in the office of the Clerk of the within named court on 19 .

Dated: Buffalo, New York,

, 19 .

RAICHLE, BANNING, WEISS & HALPERN
Attorneys for

Office and Post Office Address
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BUFFALO, NEW YORK 14203
TEL: (716) 852-7587

To:

Attorneys for

Attorneys for

Attorneys for

SERVED BY MAIL PERSONALLY

[illegible] DISTRICT OF NEW YORK

[illegible]OOSE BUSINESS FORMS, INC.,

Plaintiff,

v.

MINNESOTA MINING AND MANUFACTURING COMPANY,

Defendant.

OFFICE COPY

ANSWERS TO PLAINTIFF'S INTERROGATORIES TO DEFENDANT.

RAICHLE, BANNING, WEISS & HALPERN
Attorneys for Defendant.

Office and Post Office Address
10 LAFAYETTE SQUARE
BUFFALO, NEW YORK 14203
TEL: (716) 852-7587

Due and personal service of the within

together with notice of entry thereof is hereby admitted this 21st day of July, 1973.

Attorneys for

Attorneys for

Attorneys for

Attorneys for

(c) No response required.

IN THE UNITED STATES DISTRICT COURT
FOR THE WESTERN DISTRICT OF NEW YORK

MOORE BUSINESS FORMS, INC., Plaintiff,	)	Civil Action No.
v.	)	CIV. 1972-47
MINNESOTA MINING AND MANUFACTURING COMPANY, Defendant.	)	

OBJECTIONS TO CERTAIN OF PLAINTIFF'S INTERROGATORIES TO DEFENDANT

Now comes the defendant, by its attorneys, and objects to plaintiff's Interrogatories to defendant Nos. 12(b), 14(c), 15-19 (in part), 30, 36, 37 and 38(d). The grounds of the objections are set forth following repetition of the interrogatory to which the objection relates.

Interrogatory 12(b)

State fully with particularity whether or not defendant is performing any acts which might constitute invasion of any other property rights of plaintiff on the basis of acquiescence by plaintiff in such acts and reliance thereon by defendant.

OBJECTION:

This interrogatory is objected to in that by "any other property rights of plaintiff", plaintiff is admittedly inquiring into areas having utterly nothing to do with the issues raised by the pleadings in this case. While defendant's attorneys as presently advised know of no other areas, it would be an imposition on defendant to be required to make the investigation required as to permit full answer to this admittedly irrelevant inquiry.

(c) No response required.

Interrogatory 14(c)

Identify all documents known to or in the possession, custody or control of defendant constituting, referring or relating to each said product [which constitutes, comprises, incorporates or includes in any manner microscopic discrete rupturable capsules].

OBJECTION:

This part of Interrogatory 14 is hopelessly broad in calling for "all documents known to or in the possession, custody or control of defendant" relating to any product of defendant which "constitutes, comprises, incorporates or includes" microscopic rupturable capsules whether or not pertinent to plaintiff's patent in suit. Such request would include all manufacturing standards, marketing data, computer data, invoices, customer lists, privileged communications with counsel, etc., none of which has been shown to have any relevancy to any pleaded issue, and none of which is necessary to resolution of any pleaded issue.

Interrogatories 15-19, inclusive

Interrogatory 15

(a) State whether defendant employs persons to design, modify, improve or originate products constituting, comprising, incorporating or including microscopic discrete rupturable capsules or processes for making such products.

(b) If the answer to Interrogatory No. 15(a) is other than an unqualified negative, state the number of persons who are now so employed, identify each person who functions in a managerial capacity with respect to said employed persons, and state the exact nature and description of the duties and responsibilities of each such manager.

(c) Identify all persons who have functioned in a managerial capacity with respect to such employed persons since January 9, 1962, and state the exact nature of the duties and responsibilities of each such manager.

Interrogatory 16

(a) State whether defendant employs persons to conduct development with respect to products constituting, comprising, incorporating or including microscopic discrete rupturable capsules or processes for making such products.

(b) If the answer to Interrogatory No. 16(a) is other than an unqualified negative, state the number of persons who are now so employed, identify each person who functions in a managerial capacity with respect to said employed persons and state the exact nature of the duties and responsibilities of each such manager.

(c) Identify all persons who have functioned in a managerial capacity with respect to such employed persons since January 9, 1962, and state the exact nature of the duties and responsibilities of each such manager.

Interrogatory 17

(a) State whether defendant employs persons to manufacture products constituting, comprising, incorporating or including microscopic discrete rupturable capsules.

(b) If the answer to Interrogatory No. 17(a) is other than an unqualified negative, state the number of persons who are now so employed, identify each person who functions in a managerial capacity with respect to said employed persons and state the exact nature of the duties and responsibilities of each such manager.

(c) Identify all persons who have functioned in a managerial capacity with respect to such employed persons since January 9, 1962, and state the exact nature of the duties and responsibilities of each such manager.

Interrogatory 18

(a) State whether defendant employs persons to solicit sales of products constituting, comprising, incorporating or including microscopic discrete rupturable capsules.

(b) If the answer to Interrogatory No. 18(a) is other than an unqualified negative, state the number of persons who are now so employed, identify each person who functions in a managerial capacity with respect to said employed persons and state the exact nature of the duties and responsibilities of each such manager.

(c) Identify all persons who have functioned in a managerial capacity with respect to such employed persons since January 9, 1962, and state the exact nature of the duties and responsibilities of each such manager.

Interrogatory 19

(a) State whether defendant employs persons to prepare or conduct advertising and/or sales promotional material and campaigns with respect to products constituting, comprising, incorporating or including microscopic discrete rupturable capsules.

(b) If the answer to Interrogatory No. 19(a) is other than an unqualified negative, state the number of persons who are now so employed, identify by name, title and address each person who functions in a managerial capacity with respect to said employed persons and state the exact nature of the duties and responsibilities of each such manager.

(c) Identify all persons who have functioned in a managerial capacity with respect to such employed persons since January 9, 1962, and state the exact nature of the duties and responsibilities of each such manager.

OBJECTION:

As can be seen from these interrogatories, plaintiff Moore methodically inquires into the exact number of people defendant employs in virtually every area relating to defendant's business (design, development, manufacturing, sales and advertising), and the identification of "each person who functions in a managerial capacity with respect to said employed persons" as well as the "exact nature of the duties and responsibilities of each such manager". These interrogatories have been answered to the extent of identifying the primary managerial personnel in each of the areas so that plaintiff is in a position to proceed with specific relevant inquiries from or as developed from these personnel. Except for this, the interrogatories are unduly sweeping and request information which will not assist the lawsuit, and could only be of help to plaintiff as a competitor of defendant.

Interrogatory 30

(a) Identify all patents disclosing and/or claiming products constituting, comprising, incorporating or including microscopic discrete rupturable capsules or processes for making such products, owned by defendant or in which defendant has any rights or under which defendant manufactures, uses or sells such products, stating (1) defendant's rights in said patents, (2) the numbers of said patents, and (3) whether the patentees named thereon were employees of defendant at the time of their alleged inventions.

(b) Identify all pending and abandoned patent applications disclosing and/or claiming products constituting, comprising, incorporating or including microscopic discrete rupturable capsules or processes for making such products, owned by defendant or in which defendant has any rights or under which defendant manufactures, uses or sells products constituting, comprising, incorporating or including microscopic discrete rupturable capsules, setting forth (1) defendant's rights in said applications, (2) the serial numbers and filing dates of said applications, (3) the names of the alleged inventors of the subject matter claimed in said applications, (4) the location of copies of said applications other than at the U.S. Patent Office, and (b) the present custodian thereof.

OBJECTION:

This interrogatory is in part objected to as being outside the bounds of permissible relevancy or discovery, particularly in respect to paragraph 39)b), which inquires not only as to defendant's issued patents but into the subject matter of unissued patent applications maintained in confidence by the U.S. and foreign Patent Offices. This suit involves issues of infringement, validity and enforceability of plaintiff's patents. Defendant's patents are not in issue. Certain particular patent disclosures of defendant may be relevant (for example, for their disclosure of defendant's products and processes of manufacture herein accused). These have been listed in response to interrogatory 30. However, no basis exists for inquiry into all of defendant's patents and applications as an entire group, particularly as to the nature of (1) "defendant's rights" thereunder, (2) "the numbers of said patents", and (3) "whether the patentees named thereon were employees of defendant".

Interrogatory 36

(a) State whether defendant has knowledge of any tests performed by defendant, an agent thereof, or a third party, in which the subject of said tests has been a product identified in answer to Interrogatory No. 14 hereinbefore or any precursor or component thereof.

(b) If the answer to Interrogatory No. 36(a) is other than an unqualified negative, describe such tests in detail and identify all documents that constitute the results thereof.

(c) Identify all documents relating or referring to the tests described in answer to Interrogatory 36(b), and the present custodian thereof.

OBJECTION:

Interrogatory 36 is so broad and inclusive in respect to "knowledge of any tests" as to encompass virtually every operation, unlimited as to time, to which defendant's product

is subjected, including manufacture, quality control, distribution, marketing, sales, etc., most of which have utterly no connection with any issue in the case. If plaintiff will state with particularity those "tests" in respect to which it seeks information, defendant will evaluate such request and cooperate in giving discovery in areas which are relevant or which will lead to relevant facts.

Interrogatory 37

(a) Identify all documents not heretofore identified that are known to or in the possession of defendant referring or relating to products constituting, comprising, incorporating or including microscopic discrete rupturable capsules or processes for making such products.

(1) Marketed or used by defendant.

(2) Marketed or used by third parties.

OBJECTION:

Interrogatory 37 is objected to as being unduly sweeping in calling for "all documents not heretofore identified" relating to products employing "discrete rupturable capsules or processes for making such products". On its face, such inquiry goes far beyond any issue raised by the pleadings, but would comprehend much confidential information of plaintiff such as manufacturing techniques, manufacturing standards, marketing data, etc.

Interrogatory 38(d)

Identify all documents known to or in the possession, custody or control of defendant constituting, referring or relating to each such product or process [which constitute, incorporate, comprise or include microscopic discrete rupturable capsules or processes for making the same disclosed in U.S. Patent No. 3,516,941].

OBJECTION:

Same objection as registered above to Interrogatory 14(c).

RAICHLE, BANNING, WEISS & HALPERN

By_____
A Member of the Firm

10 Lafayette Square
Buffalo, New York 14203

Attorneys for Defendant

Of Counsel:

Edward A. Haight,
Chicago, Ill.

Stanley G. DeLaHunt,
St. Paul, Minn.

PLEASE TAKE NOTICE that a

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of which the within is a copy, was duly entered in the office of the Clerk of the within named court on 19 .

Dated: Buffalo, New York,

, 19 .

RAICHLE, BANNING, WEISS & HALPERN
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To:

Attorneys for

Attorneys for

Attorneys for

SERVED BY ☐ MAIL ☐ PERSONALLY
DATE

[redacted] DISTRICT OF NEW YORK

MOORE BUSINESS FORMS, INC.,

Plaintiff,

v.

MINNESOTA MINING AND MANUFACTURING COMPANY,

Defendant.

OFFICE COPY

OBJECTIONS TO CERTAIN OF PLAINTIFF'S INTERROGATORIES TO DEFENDANT.

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Attorneys for Defendant.

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BUFFALO, NEW YORK 14203
TEL: (716) 852-7587

Due and personal service of the within Objections together with notice of entry thereof is hereby admitted this 21st day of July, 1973.

Attorneys for

Attorneys for

Attorneys for

Attorneys for

IN THE UNITED STATES DISTRICT COURT
FOR THE WESTERN DISTRICT OF NEW YORK

MOORE BUSINESS FORMS, INC., Plaintiff, v. MINNESOTA MINING AND MANUFACTURING COMPANY, Defendant.	)	Civil Action No. CIV 1972-47

RESPONSES BY DEFENDANT TO PLAINTIFF'S INTERROGATORIES NOS. 39 TO 48 TO DEFENDANT UNDER RULE 33, F. R. CIV. P.

NOW COMES the defendant, Minnesota Mining and Manufacturing Company, by its agent, Waldo G. Bretson, and repeats and responds to plaintiff's Interrogatories Nos. 39 to 48, as follows:

Interrogatory No. 39

(a) Does defendant now or will defendant later allege that its purchase of a facility at Nekoosa, Wisconsin, in or about April, 1971, from Nekoosa-Edwards Paper Company, was an act to its detriment in support of any of the defenses of laches, estoppel or acquiescence as alleged in paragraphs 10, 11, or 12 of defendant's Answer herein?

(b) If the answer to Interrogatory No. 39(a) is other than an unqualified negative, state:

(1) The purchase price of the Nekoosa, Wisconsin facility;

(2) All products manufactured at the Nekoosa facility prior to its acquisition by defendant;

(3) All products manufactured at Nekoosa facility subsequent to such acquisition;

(4) All improvements, modifications or other changes made in said facility subsequent to said acquisition by defendant, and

(5) All sales or disposal of any part of Nekoosa facility made by defendant subsequent to said acquisition.

(c) If the answer to Interrogatory No. 39(a) is other than an unqualified negative, fully identify the subject of the acquisition by defendant of the Nekoosa, Wisconsin facility, including in such identification:

(1) The acreage of the plant;

(2) An inventory of the plant;

(3) A complete description of the structure of all buildings that comprise the plant, and

(4) A complete description of any other factors that would enable an expert to determine the market value of the plant at the time of purchase and at the present time.

(d) Identify fully all documents, including plans, drawings, reports, surveys, inventory lists, memoranda and evaluations made or received by defendant or agents for defendant with respect to the Nekoosa facility or parts thereof, including but not limited to documents referring or relating to the value of the facility at the time of said acquisition and thereafter.

ANSWER:

(a) In view of defendant's pending motion for summary judgment, it is presently anticipated that defendant will have no need to press "any of the defenses of laches, estoppel or acquiescence as alleged in paragraphs 10, 11 or 12 of defendant's Answer herein". Should the decision on the said motion for summary judgment dictate need for further response under the provisions of F.R.C.P. Rule 26(e)(2)(B) [cf. ¶E of the preamble to plaintiff's interrogatories], such will be seasonably made.

(b) No response required.

(c) No response required.

(d) No response required.

Interrogatory No. 40

(a) As presently advised, does defendant now or later intend to allege that its purchase or improvement of facilities at Decatur, Alabama, constitutes an act to its detriment in support of any of the defenses of laches, estoppel or acquiescence as alleged in paragraphs 10, 11 or 12 of Defendant's Answer herein?

(b) If the answer to Interrogatory No. 40(a) is other than an unqualified negative state:

(1) The purchase price or cost of modifications at the Decatur, Alabama facilities in preparation for and since manufacture of microscopic discrete rupturable capsules, or carbonless paper there;

(2) All products manufactured at the Decatur, Alabama facility prior to its use by defendant to manufacture said microcapsules or carbonless paper;

(3) All products manufactured at the Decatur, Alabama factility including and since defendant's first use of the facility to manufacture said microcapsules or carbonless paper;

(4) All improvements, modifications, or other changes made in said facility to enable defendant to use and continue to use said facility to manufacture said microcapsules or carbonless paper, and

(5) All sales or disposal of any part of the Decatur, Alabama facility made by defendant subsequent to said first manufacture of said microcapsules or carbonless paper.

(c) If the answer to Interrogatory No. 40(a) is other than an unqualified negative, fully identify the Decatur, Alabama facility at (A) the date defendant first commenced manufacture of said microcapsules or carbonless paper there, and (B) the present date, including in such identification at each date:

(1) The acreage of the facility;

(2) An inventory of the facility;

(3) A complete description of the structure of all buildings that comprise the facility, and particularly that portion most directly connected with the manufacture of carbonless paper or said microcapsules, and

(4) A complete description of any other factors that would enable an expert to determine the market value of the plant at said time of first manufacture and at the present time.

(d) Identify fully all documents, including plans, drawings, reports, surveys, inventory lists, memoranda and evaluations made or received by defendant or agents for defendant with respect to the Decatur, Alabama facility or parts thereof, including but not limited to documents referring or relating to the value of the facility at the time of said first manufacture and thereafter.

ANSWER:

(a) In view of defendant's pending motion for summary judgment, it is presently anticipated that defendant will have no need to press "any of the defenses of laches, estoppel or acquiescence as alleged in paragraphs 10, 11 or 12 of Defendant's Answer herein". Should the decision on the said motion for summary judgment dictate need for further response under the provisions of F.R.C.P. Rule 26(e)(2)(B) [cf. ¶E of the preamble to plaintiff's interrogatories], such will be seasonably made.

(b) No response required.

(c) No response required.

(d) No response required.

Interrogatory No. 41

(a) As presently advised, does defendant now or later intend to allege that its purchase or improvement of facilities at Cordova, Illinois, constitutes an act to its detriment in support of any of the defenses of laches, estoppel or acquiescence as alleged in paragraphs 10, 11 or 12 of Defendant's Answer herein?

(b) If the answer to Interrogatory No. 41(a) is other than an unqualified negative, state:

(1) The purchase price or cost of modifications at the Cordova, Illinois facilities in preparation for and since manufacture of microscopic discrete rupturable capsules, or carbonless paper there;

(2) All products manufactured at the Cordova, Illinois facility prior to its use by defendant to manufacture said microcapsules or carbonless paper;

(3) All products manufactured at the Cordova, Illinois facility including and since defendant's first use of the facility to manufacture said microcapsules or carbonless paper;

(4) All improvements, modifications, or other changes made in said facility to enable defendant to use and continue to use said facility to manufacture said microcapsules or carbonless paper, and

(5) All sales or disposal of any part of the Cordova, Illinois facility made by defendant subsequent to said first manufacture of said microcapsules or carbonless paper.

(c) If the answer to Interrogatory No. 41(a) is other than an unqualified negative, fully identify the Cordova, Illinois facility at (A) the date defendant first commenced manufacture of said microcapsules or carbonless paper there, and (B) the present date, including in such identification at each date:

(1) The acreage of the facility;

(2) An inventory of the facility;

(3) A complete description of the structure of all buildings that comprise the facility, and particularly that portion most directly connected with the manufacture of carbonless paper or said microcapsules, and

(4) A complete description of any other factors that would enable an expert to determine the market value of the plant at said time of first manufacture and at the present time.

(d) Identify fully all documents, including plans, drawings, reports, surveys, inventory lists, memoranda and evaluations made or received by defendant or agents for defendant with respect to the Cordova, Illinois facility or parts thereof, including but not limited to documents referring or relating to the value of the facility at the time of said first manufacture and thereafter.

ANSWER:

(a) In view of defendant's pending motion for summary judgment, it is presently anticipated that defendant will have no need to press "any of the defenses of laches, estoppel or acquiescence as alleged in paragraphs 10, 11 or 12 of Defendant's Answer herein". Should the decision on the said motion for summary judgment dictate need for further response under the provisions of F.R.C.P. Rule 26(e)(2)(B) [cf. ¶E of the preamble to plaintiff's interrogatories], such will be seasonably made.

(b) No response required.

(c) No response required.

(d) No response required.

Interrogatory No. 42

(a) As presently advised, does defendant now or later intend to allege that its purchase or improvement of facilities at Hartford City, Indiana, constitutes an act to its detriment in support of any of the defenses of laches, estoppel or acquiescence as alleged in paragraphs 10, 11 or 12 of Defendant's Answer herein?

(b) If the answer to Interrogatory No. 42(a) is other than an unqualified negative, state:

(1) The purchase price or cost of modifications at the Hartford City, Indiana facilities; in preparation for and since manufacture of microscopic discrete rupturable capsules or carbonless paper there;

(2) All products manufactured at the Hartford City, Indiana facility prior to its use by defendant to manufacture said microcapsules or carbonless paper;

(3) All products manufactured at the Hartford City, Indiana facility including and since defendant's first use of the facility to manufacture said microcapsules or carbonless paper;

(4) All improvements, modifications, or other changes made in said facility subsequent to said acquisition by defendant; and

(5) All sales or disposal of any part of the Hartford City, Indiana facility made by defendant subsequent to said first manufacture of said microcapsules or carbonless paper.

(c) If the answer to Interrogatory No. 42(a) is other than an unqualified negative, fully identify the Hartford City, Indiana facility at (A) the date defendant first commenced manufacture of said microcapsules or carbonless paper there, and (B) the present date, including in such identification at each date:

(1) The acreage of the facility;

(2) An inventory of the facility;

(3) A complete description of the structure of all buildings that comprise the facility, and particularly that portion most directly connected with the manufacture of carbonless paper or said microcapsules, and

(4) A complete description of any other factors that would enable an expert to determine the market value of the plant at said time of first manufacture and at the present time.

(d) Identify fully all documents, including plans, drawings, reports, surveys, inventory lists, memoranda and evaluations made or received by defendant or agents for defendant with respect to the Hartford City, Indiana facility or parts thereof, including but not limited to documents referring or relating to the value of the facility at the time of said first manufacture and thereafter.

ANSWER:

(a) In view of defendant's pending motion for summary judgment, it is presently anticipated that defendant will have no need to press "any of the defenses of laches, estoppel or acquiescence as alleged in paragraphs 10, 11 or 12 of Defendant's Answer herein". Should the decision on the said motion for summary judgment dictate need for further response under the provisions of F.R.C.P. Rule 26(e)(2)(B) [cf. ¶E of the preamble to plaintiff's interrogatories], such will be seasonably made.

(b) No response required.

(c) No response required.

(d) No response required.

Interrogatory No. 43

(a) As presently advised, does defendant now or later intend to allege that its purchase or improvement of facilities at locations other than Nekoosa, Wisconsin, Decatur, Alabama, Cordova, Illinois, and Hartford City, Indiana, constitutes an act to its detriment in support of any of the defenses of laches, estoppel or acquiescence as alleged in paragraphs 10, 11 or 12 of Defendant's Answer herein?

(b) If the answer to Interrogatory No. 43(a) is other than an unqualified negative, state:

(1) The name, address, and location of each such facility;

(2) The purchase price or cost of modifications of each such facility in preparation for and since manufacture of microscopic discrete rupturable capsules or carbonless paper there;

(3) All products manufactured at each facility prior to its use by defendant to manufacture said microcapsules or carbonless paper;

(4) All products manufactured at each facility including and since defendant's first use of the facility to manufacture said microcapsules or carbonless paper;

(5) All improvements, modifications, or other changes made in each facility subsequent to said acquisition or said first use by defendant; and

(6) All sales or disposal of any part of each facility made by defendant subsequent to said first manufacture of said microcapsules or carbonless paper, or acquisition.

(c) If the answer to Interrogatory No. 43(a) is other than an unqualified negative, fully identify each facility at (A) the date defendant first acquired it and/or commenced manufacture of said microcapsules or carbonless paper there, and (B) the present date, including in such identification at each date:

(1) The acreage of the facility;

(2) An inventory of the facility;

(3) A complete description of the structure of all buildings that comprise the facility, and particularly that portion most directly connected with the manufacture of carbonless paper or said microcapsules, and

(4) A complete description of any other factors that would enable an expert to determine the market value of the plant at said time of first manufacture or acquisition and at the present time.

(d) Identify fully all documents, including plans, drawings, reports, surveys, inventory lists, memoranda and evaluations made or received by defendant or agents for defendant with respect to each facility or parts thereof, including but not limited to documents referring or relating to the value of the facility at the time of said first manufacture or acquisition and thereafter.

ANSWER:

(a) In view of defendant's pending motion for summary judgment, it is presently anticipated that defendant will have no need to press "any of the defenses of laches, estoppel or acquiescence as alleged in paragraphs 10, 11 or 12 of Defendant's Answer herein". Should the decision on the said motion for summary judgment dictate need for further response under the provisions of F.R.C.P. Rule 26(e)(2)(B) [cf. ¶E of the preamble to plaintiff's interrogatories], such will be seasonably made.

(b) No response required.

(c) No response required.

(d) No response required.

Interrogatory No. 44

Objected to.

Interrogatory No. 45

Objected to.

Interrogatory No. 46

(a) Have any microscopic discrete rupturable capsules been manufactured or sold by defendant since January 1, 1962, which capsules were ultimately used in the cosmetic industry?

(b) If the answer to Interrogatory No. 46(a) is other than an unqualified negative, identify such capsules by:

(1) method of preparation of the capsules;

(2) composition of shell;

(3) composition of fill;

(4) capsule diameter;

(5) shell thickness;

(6) weight of fill as a percentage of weight of capsule;

(7) the form (e.g., free-flowing powder, slurry, etc.) in which the microcapsules were shipped to the customer, and

(8) the specific ultimate use (e.g., liquid perfume, solid perfume, etc.) made of the microcapsules by the customer.

(c) Identify all documents constituting, relating or referring to the capsules identified in answer to this interrogatory.

ANSWER:

(a) Yes, since late 1971. A total of less than $70,000 of such capsules has been sold to date.

(b) (1) The method of preparation is basically similar to that employed in the manufacture of the capsules employed in defendant's carbonless papers, but process controls are maintained so that shell thickness is only about 1/40th of the capsule diameter. Following production of the capsules, the aqueous medium in which they are formed is removed.

(2) The composition of the shell is a polymer of urea and formaldehyde.

(3) The composition of the fill is mineral oil.

(4) The capsule diameter is 25 to 40 microns.

(5) The shell thickness is in the order of one micron or less.

(6) The weight of fill is nominally 80% of the capsule weight, with the weight of the fill generally being greater than 80%.

(7) Substantially dry free-flowing powder.

(8) Not all of the uses made by the customers are known. Mainly, the capsules are mixed with other solid dry ingredients to form a cosmetic powder.

(c) Objected to.

Interrogatory No. 47

(a) Has defendant, in commercial production or laboratory tests or for any other purpose ever produced dry microcapsules suitable for use in carbonless paper?

(b) If the answer to Interrogatory No. 47(a) is other than an unqualified negative, identify:

(1) each date such dry microcapsules were made;

(2) the method of making such dry microcapsules;

(3) the reason that such dry microcapsules were made;

(4) the composition (by fill and shell) and dimensions (shell thickness and capsule diameter) of such microcapsules, and

(5) the ultimate disposition of such microcapsules.

ANSWER:

(a) As presently advised, at no time from the inception of its commercialization in 1962 of "Action" brand carbonless paper (now Type 100) has defendant ever made carbonless paper, whether in commercial products, laboratory tests or for any other

purpose, from microcapsules in, or which at any time were in, dry form. During this time, defendant produced microcapsules in dry form which contained imaging components. Thus, in quality control procedures in connection with commercial capsule manufacture, defendant periodically removes a small portion of capsule slurry from the process and reduces it to dryness. But whether "such dry microcapsules" are or were "suitable for use in carbonless paper" is a matter of subjective opinion, as it was not done and hence no carbonless paper was evaluated.

(b) Answering as to the dried microcapsules resulting from the quality control procedures (there being no antecedent in the answer to part (a) for "such dry microcapsules"),

(1) As a matter of practice, in recent years quality control samples have been taken from one out of approximately every ten batches of microcapsules manufactured for defendant's Type 100 carbonless papers, and from one out of approximately every three batches of microcapsules manufactured for defendant's Type 200 carbonless papers. In earlier years, the samples were taken more frequently, sometimes from each batch. Several batches ordinarily are made each production day.

(2) In one procedure, approximately a six to eight gram aliquot portion of slurry (capsules plus aqueous medium) is removed from the commercial slurry, weighed, poured onto a tared filter paper, water-washed under a partial vacuum, and oven-dried, following which the filter and filter cake are weighed (about 2 grams).

In a second procedure, approximately a six to eight gram aliquot portion of slurry (capsules plus aqueous medium) is removed from the commercial slurry, weighed into a tared dish and oven-dried therein, following which the dish and dried solids are weighed.

(3) The reasons are to determine percent capsules and percent total solids, respectively, in the commercial slurry, so that in further processing considerations, components (though in a slurry state) may be referred to "on a dry basis".

(4) No determination of composition or dimensions of the microcapsules, either of the dried filter cake or the dish deposit, is made, but the capsules removed from the commercial slurry have the same composition and dimensions as do the slurried capsules actually finding their way into defendant's carbonless papers.

(5) From both procedures the samples are discarded, that is, the filter and filter cake from the first procedure, and the dish and contents from the second procedure.

Interrogatory No. 48

(a) Has defendant ever conducted any tests to determine the physical and/or chemical properties of microcapsules it has produced either on a commercial basis or as laboratory samples?

(b) If the answer to Interrogatory No. 48(a) is other than an unqualified negative, fully identify all such test results by date, form (e.g., notebook pages) and persons who made the tests.

ANSWER:

(a) Yes.

(b) Objected to.

* * * * *

In respect to the request in Preamble ¶D to plaintiff's interrogatories, the following response is made as to interrogatories herein answered:

(1) It would be virtually impossible for defendant to determine and list each person having some "knowledge with respect to the matter about which the inquiry is made". Persons believed by defendant to have substantial knowledge, and who could identify

others in respect to specific areas of inquiry where relevant, are as follows:

Interrogatories Nos. 39-43: Defendant's attorneys in consultation with Carl A. Kuhrmeyer, Group Vice President of defendant, and Waldo G. Bretson, General Manager of the Paper Products Division of defendant.

Interrogatory No. 46: Darrell K. Huebner
Dean A. Ostlie
Norman P. Sweeney

Interrogatories Nos. 47-48: Alva L. Frye
Donald E. Disselkamp
Dean A. Ostlie
Wayne O. Otteson
Buck Stricklin
Claude F. Vincent

(2) Persons furnishing information on which answers are based are:

Interrogatories Nos. 39-43: Carl A. Kuhrmeyer
Waldo G. Bretson

Interrogatory No. 46: Dean A. Ostlie
Keith E. Relyea
Norman P. Sweeney

Interrogatories Nos. 47-48: Dean A. Ostlie
Claude F. Vincent

(3) No individuals are "named in response" to Interrogatories 39-48.

Waldo G. Bretson
Waldo G. Bretson

STATE OF MINNESOTA)
COUNTY OF RAMSEY) ss.

The said WALDO G. BRETSON, known to me, did appear before me this 13th day of July, 1973, and swore to the above responses being correct to the best of his knowledge and belief.

Notary Public

MARJORIE E. ROUB, Notary Public, Ramsey County, Minn. My Commission Expires Oct. 25, 19

CERTIFICATE OF SERVICE

I hereby certify that on the 17th day of July, 1973, the foregoing "Responses by Defendant to Plaintiff's Interrogatories Nos. 39 to 48 to Defendant under Rule 33, F.R. Civ. P." was served on plaintiff, Moore Business Forms, Inc., by sending copies thereof to Walter D. Ames, Esq., Watson, Cole, Grindle & Watson, 815 Fifteenth Street, N.W., Washington, D. C. 20005, and Thomas J. Hanifin, Jr., Esq., Cohen, Swados, Wright, Hanifin & Bradford, 256 Third Street, Niagara Falls, New York 14303, attorneys for plaintiff, by prepaid first class mail.

Gary L. Griswold

IN THE UNITED STATES DISTRICT COURT
FOR THE WESTERN DISTRICT OF NEW YORK

MOORE BUSINESS FORMS, INC., Plaintiff,	)	
v.	)	Civil Action
MINNESOTA MINING AND MANUFACTURING COMPANY, Defendant.	)	No. CIV 1972-47

OBJECTIONS TO CERTAIN OF PLAINTIFF'S INTERROGATORIES TO DEFENDANT

NOW COMES the defendant, by its attorneys, and objects to plaintiff's interrogatories to defendant Nos. 44, 45, 46(c) and 48(b). Interrogatories 39-43, 46(a), 46(b) and 48(a) are being answered contemporaneously herewith. The grounds for the objections are set forth following repetition of the objected to interrogatories:

Interrogatory No. 44

Identify fully each and every document constituting, relating or referring to research in the production, uses and properties of microscopic discrete rupturable capsules and carbonless paper conducted by defendant prior to its marketing of Type 100 paper in 1962, specifically including but not limiting such identification to the research notebooks of Dr. Gale W. Matson and Dr. Walter J. Bublitz, Jr., and all reports by superiors of Drs. Matson and Bublitz relating to their work on said microcapsules and carbonless paper.

Interrogatory No. 45

Identify fully each and every report or informative document relating or referring to microscopic discrete rupturable capsules or carbonless paper since January 1, 1962, addressed to or signed by:

(a) Waldo G. Bretson, general manager of the Paper Products Division;

(b) R. C. Bertelson, manufacturing manager of the Division, or any predecessor in such position,

(c) B. Stricklin, technical director of the Division, or any predecessor in such position, and

(d) D. K. Huebner, microfragrance market development manager, or any predecessor in such position.

Interrogatory No. 46(c)

Identify all documents constituting, relating or referring to the capsules identified in answer to this interrogatory.

[For reference in understanding this interrogatory, parts (a) and (b) of Interrogatory 46, which have been answered, read:

(a) Have any microscopic discrete rupturable capsules been manufactured or sold by defendant since January 1, 1962, which capsules were ultimately used in the cosmetic industry?

(b) If the answer to Interrogatory No. 46(a) is other than an unqualified negative, identify such capsules by:

(1) method of preparation of the capsules;

(2) composition of shell;

(3) composition of fill;

(4) capsule diameter;

(5) shell thickness;

(6) weight of fill as a percentage of weight of capsule;

(7) the form (e.g., free-flowing powder, slurry, etc.) in which the microcapsules were shipped to the customer, and

(8) the specific ultimate use (e.g., liquid perfume, solid perfume, etc.) made of the microcapsules by the customer.]

Interrogatory No. 48(b)

If the answer to Interrogatory No. 48(a) is other than an unqualified negative, fully identify all such test results by date, form (e.g., notebook pages) and persons who made the tests.

[For reference in understanding this interrogatory, part (a), which has been answered, read:

(a) Has defendant ever conducted any tests to determine the physical and/or chemical properties of microcapsules it has produced either on a commercial basis or as laboratory samples?]

These interrogatories are objected to as being hopelessly broad and sweeping in indiscriminately seeking the identification of thousands upon thousands of documents without regard to whether they have any bearing on or relevance to the subject matter involved in the pending action". [Cf. F.R.C.P. 26(b)(1).]

Thus, interrogatory 44 seeks "each and every document constituting, relating or referring" to defendant's research on microcapsules and carbonless paper prior to 1962 when defendant commenced commercialization. (This patent infringement suit, not filed until a decade later in January, 1972, is governed by a six-year statute of limitations.)

Not content with all research documents prior to 1962, interrogatory 45 asks for "each and every report or informative document" issued since January 1, 1962 relating to microcapsules or carbonless paper, which was addressed to or signed by four key persons in defendant's involved division, and "any predecessor" of such persons.

Between these two interrogatories, nearly every report or piece of correspondence generated before and since 1962 in any way relating to microcapsules or carbonless paper seems to be called for.

Additionally, by reference to the definition of "microscopic discrete rupturable capsules" in preamble B to the interrogatories, plaintiff evidences its intention to include within their scope subject matter not in the slightest confined to that of its patent in suit. And by the definition of "documents" in preamble C, plaintiff demands identification of every scrap or record ever existing, without regard, for example, to whether such still exists, so as to be susceptible of identification at this date, or whether it is duplicative or stored in computers.

Interrogatory 46(c), which obviously duplicates a portion of interrogatories 44 and 45, seeks virtually every document ever generated having relation to microcapsules of defendant which were "ultimately used in the cosmetic industry", again without regard to whether such have any relation to plaintiff's patent, in respect to which no charge of infringement has been leveled.

Interrogatory 48(b), in respect to "any tests to determine the physical and/or chemical properties" of any and all microcapsules ever produced by defendant (without regard to any issue in the case), seeks all "test results by date, form (e.g., notebook pages) and persons who made the tests".

ALEXANDER, SELL, STELDT & DELAHUNT

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A Member of the Firm

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Dated at St. Paul, Minnesota
July 17, 1973

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815 Fifteenth Street, N.W.
Washington, D. C. 20005

Attorneys for Plaintiff

CERTIFICATE OF SERVICE

I hereby certify that on the 17th day of July, 1973, the foregoing "Objections to Certain of Plaintiff's Interrogatories to Defendant" was served on plaintiff, Moore Business Forms, Inc., by sending copies thereof to Walter D. Ames, Esq., Watson, Cole, Grindle & Watson, 815 Fifteenth Street, N.W., Washington, D. C. 20005, and Thomas J. Hanifin, Jr., Esq., Cohen, Swados, Wright, Hanifin & Bradford, 256 Third Street, Niagara Falls, New York 14303, attorneys for plaintiff, by prepaid first class mail.

Gary L. Griswold

Gary L. Griswold

IN THE UNITED STATES DISTRICT COURT
FOR THE WESTERN DISTRICT OF NEW YORK

MOORE BUSINESS FORMS, INC., Plaintiff, v. MINNESOTA MINING AND MANUFACTURING COMPANY, Defendant.	)	Civil Action No. CIV 1972-47

AFFIDAVIT OF STANLEY G. DELAHUNT
IN SUPPORT OF DEFENDANT'S
MOTION FOR SUMMARY JUDGMENT

STATE OF MINNESOTA)
) ss.
COUNTY OF RAMSEY)

STANLEY G. DELAHUNT, being first duly sworn, deposes and states as follows:

1. I am an attorney at law and of counsel for defendant in the above-captioned action.

2. Annexed hereto as Exhibit A is a copy of Macaulay Patent No. 3,016,308 in suit, said patent being granted January 9, 1962 to the said plaintiff, Moore Business Forms, Inc., on application Serial No. 676,574 filed August 6, 1957.

3. Annexed hereto as Exhibit B is a copy of certain interrogatories propounded by defendant to plaintiff, and plaintiff's answers thereto, namely, Interrogatories Nos. 1, 2(a), 3(a), 6(a) and 9(a). Said answers show that in this suit defendant is charged with having infringed claims 8, 11-13, 16, 17 and 22-29 of the Macaulay patent in suit.

4. The interrogatory answers collected as Exhibit B hereto also reveal that the only product of defendant presently charged by plaintiff as an infringement, or the manufacture of

which or any component of which is charged as an infringement of the Macauley patent, is defendant's Type 200 carbonless paper.

5. Annexed hereto as Exhibit C is page 122 of the deposition of plaintiff's employee, Dr. Norman Macauley, patentee of Macauley Patent No. 3,016,308 in suit, said deposition having been taken by defendant in this case April 5-6, 1973.

6. Annexed hereto as Exhibit D are pages 14-19, 22-24 and 67-68 of the deposition of plaintiff's employee, Chien J. Yeh, taken by defendant on April 4, 1973. Mr. Yeh is plaintiff's Manager, Process Engineering, and was identified by plaintiff as the person knowing most about the make-up of plaintiff's recently introduced "MCP" carbonless paper.

7. Annexed hereto as Exhibit E is a copy of Ruus Patent No. 3,429,827, granted to Moore Business Forms on February 25, 1969, marked in the aforesaid Yeh deposition as defendant's Yeh Deposition Exhibit 11 for identification.

8. Annexed hereto as Exhibit F are pages 61-62 of the deposition of plaintiff's Vice President and Director of Research, Robert H. Downie, taken by defendant on April 4, 1973.

9. Annexed hereto as Exhibit G is a copy of the proceedings in the United States Patent Office ("File Wrapper and Contents") of Application Serial No. 676,574 aforesaid, upon which was granted the Macauley Patent No. 3,016,308 in suit.

Further affiant sayeth not.

Stanley G. DeLaHunt

Subscribed and sworn to before
me this 29th day of June, 1973.

CERTAIN INTERROGATORIES PROPOUNDED BY DEFENDANT TO PLAINTIFF AND ANSWERS THERETO

Interrogatory No. 1

1. Specify each claim of Macauley Patent No. 3,016,308 in tuis which defendant is charged with having infringed.

Answer

As presently advised, it is plaintiff's contention that defendant has infringed or is presently infringing at least claims 8, 11, 12, 13, 16, 17, 22, 23, 24, 25, 26, 27, 28 and 29 of United States Letters Patent No. 3,016,308. In view of the fact that discovery in this litigation is just commencing and further in view of the fact that much of the factual information relating to infringement is within the possession and control of defendant, it is possible, that as discovery proceeds, it will be determined that other claims of United States Letters Patent No. 3,016,308 are infringed and/or that one or more of the above enumerated claims are not infringed.

* * * *

Interrogatory No. 2(a)

2.(a) In respect to each of the claims within the group of claims 1-10, inclusive, specified in the answer to Interrogatory No. 1, identify all products of defendant, including any component of which (identifying same) plaintiff contends to have been made by a process infringing such claim.

Answer

(a) As presently advised, it is plaintiff's contention that at least defendant's Type 200 carbonless paper is made by an infringing process.

* * * *

Interrogatory No. 3(a)

3.(a) In respect to each of the claims within the group of claims 11-22, inclusive, specified in the answer to Interrogatory No. 1, identify all products of defendant, including trade designation and type number, which plaintiff contends infringes or any component of which plaintiff contends at any stage infringed such claim.

Answer

(a) As presently advised, it is plaintiff's contention that at least defendant's Type 200 carbonless paper constitutes an infringement of or includes a component which infringes each of claims 11, 12, 13, 16, 17, 22, 23, 24, 25, 26, 27, 28 and 29 of United States Letters Patent 3,016,308.

* * * *

Interrogatory No. 6(a)

6.(a) In respect to each of claims 23 and 24 specified in the answer to Interrogatory No. 1, identify all record copying sheets of defendant charged to infringe.

Answer

(a) As presently advised, it is plaintiff's contention that defendant's Type 200 carbonless paper can be utilized as record copying sheets and infringes claims 23 and 24 of United States Patent 3,016,308.

* * * *

Interrogatory No. 9(a)

9.(a) In respect to each of the claims within the group of claims 25-29, inclusive, specified in the answer to Interrogatory No. 1, identify all papers of defendant, including trade designation and type number, charged to infringe such claim.

Answer

(a) As presently advised it is plaintiff's contention that defendant's Type 200 carbonless paper infringes claims 25 to 29, inclusive, of United States Letters Patent 3,016,308.

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A. This one?

Q. Yes, the Macaulay patent here in suit.

A. Yes.

Q. That issued in 1962, did it not?

A. Yes.

Q. And wasn't that kind of a red letter day in your career when that patent issued?

A. In a sense, yes but if I can explain, prior to this date and through the whole development, the major objective or one of our major objectives as to developing a proprietary carbonless paper, was to avoid the existing patents.

Q. Well, let's go back to your patent. Your patent was basically on free-flowing capsules, was it not?

A. Correct.

Q. And products made using such capsules.

A. Correct.

Q. And it issued in 1962.

A. Correct.

Q. And Action Paper came on the scene in around 1963.

A. I will take your word for it.

Q. Well, didn't we agree yesterday that that was generally the point in time when you encountered

A. He was Manager of Chemical Development.
Q. What was that assignment?
A. That assignment was to develop the process for making the carbonless system.
Q. Now, was this to be any kind of a carbonless system that you saw fit to select or was it to be a particular type of carbon system?
A. This was a particular type.
Q. What type?
A. Well, I think this is - - involves secrets. I can't answer that.
Q. Did it involve encapsulation?
A. Yes.
Q. Did Dr. Macaulay, as part of his project assignment, direct that your process development work be in connection with a carbonless paper involving encapsulation technology?
A. Yes.
Q. Have any patents issued to the Moore Company as a consequence of that project, Mr. Yeh?
A. Not from my work.
Q. Did your project lead to a commercial product?
A. Yes.

Q. And what is that product?

A. That particular product is Moore Carbonless Paper.

Q. Known as MCP Paper?

A. MCP, right.

Q. And is MCP Paper a commercial product of your company today?

A. Yes, so far as I know.

Q. And when was the product first commercialized, to your knowledge?

MR. AMES: You mean, "sold" by "commercialized?"

MR. DELAHUNT: Well, let's see if the witness can answer.

MR. AMES: If you understand the question, you can answer.

A. I am not quite sure. I am not involved with the market. So, I couldn't tell you that definitely.

Q. Does MCP Paper, as a commercial product today, involve a full line of carbonless paper products?

A. I don't know what your definition of "Moore line" is?

Q. Well, carbonless paper is primarily of the MCP type, is primarily used as a manifolding paper, is it not, what you consider manifolding paper?

A. Yes.
Q. And does not the industry require a manifolding paper system to be madeup of various colors?
A. You mean the paper or the image color?
Q. The paper color.
A. Yes.
Q. Does Moore's MCP Paper as of this date carry the full line of colors ordinarily required by industry for manifolding paper?
A. Yes.
Q. And how long has that been the case?
A. I still cannot remember the date. I don't get involved with that.
Q. Well, can we agree it has just been within the last six months?
A. Maybe even longer. I don't know exactly.
MR. DELAHUNT: Okay. I hand the reporter a document entitled, "Sales Bulletin, Moore Business Forms, Inc., Central Division" dated April 30th, 1970 and ask the reporter to mark the document as Defendant Yeh Deposition Exhibit 8 for identification.
(Whereupon, the above-mentioned document

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was marked Defendant Yeh Exhibit 8 for identification.)

BY MR. DELAHUNT:

Q. Mr. Yeh, do you recognize this document as a document of your company?

A. Yes. It says so there.

Q. This document is dated April 30th, 1972 and appears to be an announcement of the MCP Paper, do you note that?

A. Yes. That is what the document says, yes.

Q. Does that date help you in respect to when the MCP Paper became a commercial product with your company?

A. I assume so.

Q. Now, were you aware that at sometime around the spring of 1972, MCP Paper was announced as a commercial product?

A. I heard they were planning to make an announcement sometime. I don't know which announcement that would be.

Q. But does your recollection as to when that was, accord with the April date on Yeh Exhibit 8?

A. Well, if Exhibit 8 says April 30th, that would be

right.

Q. Now, at that time, did the product line marketed under the brand MCP Paper, include all of the colors?

MR. AMES: If you know.

A. I don't know. At that time, I don't know.

Q. All right. Do you know whether the product was announced by Moore at a time before your company possessed a full line of products of the MCP type?

A. I don't know exactly what your question is. I don't understand that. The Moore Company made an announcement. They also planned to have a full line of paper, no matter, you know, when they make an announcement.

Q. Have you seen the commercial product of your company, MCP Paper?

A. Yes.

Q. Does it carry a patent marking on it?

A. Yes. I saw that.

Q. How many patents are carried on the marking?

A. I have to look it up. I don't remember.

Q. Is there more than one?

A. I don't know.

Q. How would you determine that information?
A. Well, I just look it up in the form. They have a line printed with the patent number.'
Q. Do you recall any patent number by either number or name that is carried on the literature that you referred to?
A. I don't recall that.
Q. How long would it take if we adjourned right now to secure one of the pieces of paper that you are referring to which does show the patent number?
A. Well, it will only take a few minutes.
MR. DELAHUNT: May I suggest, Mr. Ames, that we take a short recess and do that? We want to make the testimony as certain as we can.
MR. AMES: Well, you know, Mr. Delahunt, you have taken this witness who is in Product Development and you are asking him questions about marketing. Mr. Allen yesterday was a marketing man and you asked him questions about research. I have no objection at a later time of producing a sample of MCP Paper, whatever is commercial but this witness does not

it. Thank you.

BY MR. DELAHUNT:

Q. Would you identify the object that you have just handed me, Mr. Yeh?

A. This is one of the MCP products.

Q. And this is what you referred to in your earlier answer as a form?

A. Right.

Q. This form contains four sheets, does it not?

A. We call this the four part form, four part contiguous form.

MR. DELAHUNT: I will ask the reporter to mark the four part form the witness has produced as Yeh Deposition Exhibit 9 for identification.

(Whereupon, the above-mentioned document was marked Defendant Yeh Exhibit 9 for identification.)

BY MR. DELAHUNT:

Q. Mr. Yeh, does the form, Exhibit 9, carry on it any patent marking?

A. Yes.

Q. And does the marking appear at the portion, the

margin of the sheet just before the reporter's mark?
A. Yes.
Q. And does that say "MCP I, Moore Business Form, Inc., Patent No. 3,429,827?"
A. Yes.
Q. Do you find any other patent marking on the product?
A. No.
Q. Do you know of any other patent marking which has been carried on the product?
A. I don't know.
Q. Do you know of any - -
A. I don't get involved with this patent province so I don't know.
Q. Who is it, if you know, that does get involved in the question of patent marking?
A. Well, I would assume that is some of our Patent Department's responsibility. We have a Patent Department here.
MR. AMES: Is that Mr. Hageman and Mr. Knudsen?
MR. DELAHUNT: Is Mr. Hageman an attorney, Mr. Ames?
MR. AMES: No, he is not, sir.
MR. DELAHUNT: But he is in the Patent Department, is he?

MR. AMES: Yes. The Patent Department, to the best of my knowledge, consists of Mr. Andrew H. Hageman and Mr. James B. Knudsen.

BY MR. DELAHUNT:

Q. Do you recognize the patent number that appears on Exhibit 9, Mr. Yeh, as being a patent of the Moore Company?

A. Well, we have a patent number there. I am sure I would consider this a Moore patent number, yes.

Q. I understand that Patent No. 3,429,827 is a patent in the name of Henn Ruus granted February 25th, 1969 on application applied for November 23, 1962. The patent being assigned to Moore Business Forms, Inc. Are you familiar with the Ruus patent?

A. Not very familiar with it.

Q. Have you seen the Ruus patent?

A. Yes. I read it briefly a long time ago.

Q. When did you read it?

A. I don't know. I don't recall the exact date.

Q. Well, as I understand it, Dr. Macaulay assigned you the project which led to MCP Paper?

A. Yes.

Q. In 1967, is that correct, sir?

A. No.
Q. What is a free flowing powder?
A. Well, my definition is a solid, you know, not in liquid form.
Q. Not in liquid form?
A. No.
Q. And a powder is in dry form.
A. Right.
Q. Like ordinary table salt. You pour it out of the cellar, it is in the form of a free flowing powder, is it not?
A. Right.
Q. Or it is supposed to be.
A. Right.
MR. AMES: If that is a free flowing powder, that would be unusual. The witness hasn't been qualified as an expert in the field of powders.
Q. What is there in Example 1 that tells you the material is not isolated to a free flowing powder?
A. I didn't say.
Q. I see. Now, from that do you infer in the example

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that the capsules were retained in a liquid system?

A. Yes.

Q. Is that a part of the procedure that is common also to MCP Paper?

A. Yes.

Q. In other words, in the manufacture of the MCP Paper, the capsules are maintained in a liquid system for their coating on the paper substrate, correct, sir?

A. Yes.

Q. Mr. Yeh, do you draw a distinction in your mind between a record copying sheet having on one surface, a coating of capsules and a papar having on one surface a coating of those same kind of capsules?

A. I don't understand your question.

Q. Well, in your mind, do you see a difference between the record copying sheet as described and the paper I described?

MR. AMES: Did you describe a record copying sheet?

MR. DELAHUNT: I described - - I referred to a record copying sheet having on it at least a portion of one side thereof, a coating

T-100 12-28-70 →

EXHIBIT A
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Feb. 25, 1969 H. RUUS 3,429,827

METHOD OF ENCAPSULATION

Filed Nov. 23, 1962

FIG. 1

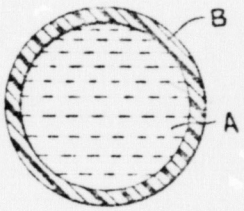


FIG. 2

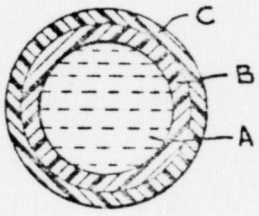


FIG. 3

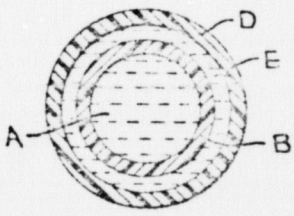
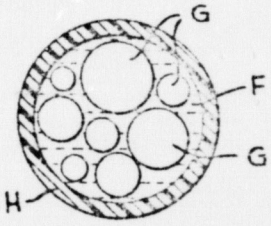


FIG. 4



INVENTOR,
HENN RUUS

BY Watson, Cole, Grindle & Watson
ATTORNEYS

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United States Patent Office

3,429,827

Patented Feb. 25, 1969

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3,429,827

METHOD OF ENCAPSULATION

Henn Raus, Niagara Falls, N.Y., assignor to Moore Business Forms, Inc., Niagara, Falls, N.Y., a corporation of Delaware

Filed Nov. 23, 1962, Ser. No. 239,732

U.S. Cl. 252—316 7 Claims

Int. Cl. B01j 13/02

This invention relates to a process of encapsulation and to novel encapsulated substances. More particularly, the invention embraces an encapsulated substance having a shell of insoluble, infusible, high molecular weight condensation polymer. The encapsulating process comprises division and dispersion of the substance to be encapsulated as a discontinuous phase, within a continuous fluid phase. Each phase must contain an intermediate or an intermediate must be added, which will react with the intermediate in the other phase to form a continuous high molecular weight condensation polymer film at the interface of the two phases. The dispersed substance is enclosed within the polymer film.

The art of encapsulation has been the object of considerable attention in recent years in view of the increased need to maintain a reactive material in an inert stage until such time as it is called upon to perform a given function. Thus, inertness is provided by interposing, by encapsulation, a non-reactive barrier or shell between the reactive material and its immediate surrounding. Removal of the barrier or shell by any suitable means "activates" the encapsulated substance. In this manner, the handling properties of solids can be conferred on liquids and gases. Adhesives can be made non-adhesive until adherence is required and reactive chemicals can be maintained inactive until such time as their reactivity is released. Flammable substances can be rendered non-flammable while being transported or during storage, but readily released unchanged when desired.

More specifically, the technique of encapsulation is employed effectively in the manufacture of manifold paper where a thin layer of microscopic capsules containing a suitable marking substance are bonded to a pliable sheet. The marking substance is maintained inactive until the capsules are ruptured by pressure of a stylus or other means. Encapsulated substances are useful in the preparation of drugs where a delayed effect is desired. Thus, the active ingredient can be coated with a suitable protective layer and when the drug is taken internally, it will not immediately affect the patient but remains inactive until the polymer layer is dissolved. As is apparent, depending on the encapsulating substance, the influence of the drug can be delayed from a matter of minutes up to several hours. The encapsulation technique can also be used in the preparation of pressure sensitive adhesives for application to placards, envelopes, etc. where it is necessary that the surface remain non-adhesive until adherence is desired. By employing encapsulating substances, it is not necessary to wet the surface but adherency is obtained by merely applying pressure.

Several methods are presently known for micro-encapsulation. Thus, Green U.S. Patent No. 2,712,507 describes the encapsulation of a hydrophilic oil by gelatin and gelatin-gum arabic complexes utilizing a "coacervation" process. The process is limited to water-soluble hydrophilic colloids and cannot be used for encapsulation of water or water-soluble substances. Moreover, materials which are sensitive to the acid pH of the process are inoperable. Brynko U.S. Patent No. 2,969,330 discloses encapsulation by an addition polymerization process whereby at least one selected monomer is dissolved in an oil in which the solid polymer material is insoluble. The solution is then dispersed as droplets in a polar liquid where

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polymerization occurs due to the influence of a catalyst which can be introduced in any of the phases. The polymer material deposits at the interface of the oil droplets and polar liquids forming an individual solid wall around each oil droplet resulting in discrete, pressure rupturable, substantially spherical, oil-containing capsules. However, again the process described excludes encapsulation of water-soluble materials. Macaulay U.S. Patent No. 3,016,308 enumerates a wide range of substances encapsulated by a variety of film formers. The suspension-evaporation method described can be used for encapsulation with polymers which are soluble in suitable solvents. For high molecular weight polymers, however, available solvents are very limited and solution viscosities high, substantially limiting the process as a practical matter.

Accordingly, it is an object of the instant invention to provide a simplified method of encapsulation wherein the capsule shell consists of a high molecular weight condensation polymer.

It is another object of the instant invention to provide a simplified method of encapsulating water or water-soluble substances.

It is another object of this invention to provide an encapsulated product having an insoluble and infusible polymer shell.

It is another object of the instant invention to provide an encapsulated product wherein the product is water or an aqueous solution or dispersion.

It is another object of this invention to provide an encapsulated product having high uniformity of thickness of the polymeric capsule shell.

It is another object of the instant invention to provide a dry, free-flowing, discrete microscopic capsule.

It is another object of the instant invention to provide an improved manifold paper having microscopic, pressure rupturable capsules on at least one surface thereof, wherein the capsule shell consists of a high molecular weight condensation polymer such as a polyamide, polyester, polyurethane, polysulfonamides, etc.

These and other objects of the instant invention will become more fully apparent from the following detailed description with particular emphasis being placed on the examples and annexed drawing.

In general, the objects of the present invention are accomplished by utilizing a modification of the known interfacial polycondensation technique. Such techniques are thoroughly described in the literature, with the article entitled "Interfacial Polycondensation, a Versatile Method of Polymer Preparation," by P. W. Morgan, Society Plastics Engineers Journal, 15, 485-495 (1959) providing a good summary of the reactions involved and the polymers which can be prepared by this method. Magat et al. U.S. Patent No. 2,708,617 also describes the technique. Essentially, the process comprises bringing two reactants together at a reaction interface where polycondensation occurs substantially instantaneously to form a thin film which is insoluble in the parent media of the reactants. The interface can be temporary or permanent. If the reactants are dissolved separately in two mutually soluble media and one medium dispersed within the other, the rate of the condensation may be of such speed that the insoluble film is formed before substantial solution of one medium in the other occurs, the thin polymer film formed, thereafter, preventing further mutual solution of the media.

The preferred and mechanically most simple method of providing the interface for encapsulation is to disperse or emulsify one reactant for the condensation polymer in a continuous phase containing the second reactant. The substance to be encapsulated will also be contained in the dispersed phase. However, in order to more accurately

control the formation of the capsules, it can be convenient to emulsify or disperse one reactant for the condensation polymer, together with the substance to be encapsulated in a continuous phase and thereafter add additional continuous phase containing the second reactant to the dispersion. The polycondensation polymer shell will form at the interface of the dispersed substance and encapsulate the material. The dispersion or emulsion can be stabilized by addition of surface active agents, or protective colloids to the continuous phase.

The dispersion or emulsion can be produced by the standard suspension and emulsification techniques known in the art. Thus, emulsions or dispersions can be prepared by agitation, preferably in the presence of one or more emulsifying agents. The efficiency of the emulsification depends among other factors, on the type and degree of agitation and the manner in which the emulsifying agent is introduced. The primary function of the agitation is to break up both phases of the emulsion so that the one which will become the dispersed phase is able to form small globules. The emulsifier is employed to lower the interfacial tension since the lower the interfacial tension the lower the amount of mechanical energy needed to break up the phases. Where the interfacial tension of a system is extremely low, spontaneous emulsification may result. The preparation of the emulsions can be facilitated by various types of colloid mills and homogenizers engineered to obtain maximum shear action of the fluid and enhance the formation of fine uniform globules.

Emulsifying agents which are operable in preparing the emulsions or dispersions include the long chain polar and non-polar compounds, as well as the more complex hydrophilic colloids, such as gums, starches, proteins, etc. which are known to be readily adsorbed at the phase interfaces.

In addition to simple agitation with or without emulsifier, the dispersion can be formed by injecting one phase into a second phase from an orifice at a rate designed to exceed the critical velocity required for continuous flow. A solid phase containing one reactant may be dispersed into a continuous medium containing the second reactant. The continuous medium may contain the second reactant or a solution of the second reactant also as a discontinuous phase. Such would be the case when a liquid or solid medium containing the first reactant is dispersed into a continuous gaseous phase containing a fine dispersion of the second reactant. The effective reactive area of the second reactant can be increased by reducing the particle size of its dispersion.

Capsules having a wide variety of structures can be prepared by the process of the instant invention. Thus, FIGURES 1-4 of the drawing are representative of the final structures possible but are not to be construed as being limiting. In the drawing,

FIGURE 1 illustrates a capsule wherein A is the encapsulated material and B is a shell of high molecular weight polymer, produced by interfacial polycondensation.

FIGURE 2 depicts a capsule wherein A is the encapsulated material, B is the shell composed of a high molecular weight polymer produced by interfacial polycondensation and C is a second shell which is applied by a spray drying process, or similar technique or coating a dry particulate substance.

In FIGURE 3, A is the encapsulated material, B is a polymer shell formed by interfacial polycondensation and E represents a second phase which may be similar to or different from A. D represents a second condensation polymer shell, which may be the same as or different from B.

In FIGURE 4, G represents the capsules of FIGURES 1, 2 or 3, F is a dispersion medium for capsules G, and H represents an interfacial polymer shell.

Virtually any material can be encapsulated by the instant process, provided reasonable precautions are exercised to avoid selecting materials which tend to interfere with the interfacial polycondensation reaction. However, by judicious selection of the reactants to take part in the polycondensation, bearing in mind the nature of the material to be encapsulated, no problem will be encountered. Thus, the substances to be encapsulated can be gases, liquids or solids which are water-insoluble or water-soluble. As noted hereinbefore, in the prior art methods, it has not been possible to encapsulate water or water-soluble substances. However, in accordance with the instant invention, water and water-soluble substances can be encapsulated by at least two methods. Thus, a solution of water and a reactant can be extruded into a solution of the second reactant for the condensation polymer, forming small droplets of water within the solution and instantaneously encasing the droplets by the formation of condensation polymer at the interface. The second method comprises forming a water-in-oil emulsion or dispersion and thereafter adding a solution of the second reactant. The reaction of the two reactants at the interface will encase the water or water-soluble substance within a polymer shell.

As is apparent, water-insoluble materials can be encapsulated by the reverse of the technique described hereinbefore. According to the instant invention, volatile liquids such as toluene, xylene, methyl ethyl ketone can be encapsulated in polyamide polymer shell, as well as non-volatile liquids such as methyl phthalyl ethyl glycolate. Additionally, reactive substances such as acids, alkaline materials, activated monomers, i.e., monomers in the presence of a catalyst, can be encapsulated in a polycondensation shell of a high molecular weight polyamide or polyurethane. Polyesters can be employed to encapsulate volatile liquids such as toluene or xylene, as well as flammable liquids.

Depending upon the ultimate use of the encapsulated materials, it may be desirable to have more than one layer of "active" substance coated with one or more polymer layers. Systems of this type have been described and illustrated in FIGURE 3 of the drawing.

Thus, in the preparation of drugs, it can be desirable to encapsulate an "active" substance and thereafter, enclose a thin layer of a second substance around the first capsule, which may be less "active" or have a counteracting effect for the initial encapsulated substance. As is apparent, if the instant process is employed to encapsulate drugs, the polymer and carriers selected must necessarily be non-toxic.

Additionally, it may be desirable to re-coat the original encapsulated substances with a heavier coating, employing methods commonly known in the art. One such method would be to suspend the discrete microcapsules in a column of air and spray a liquid encapsulating substance, onto the particles. The particles, being suspended in air and in constant motion, will not unduly agglomerate and will be evenly coated with the encapsulating substance. Another method is to spray the discrete capsules with a suitable adhesive material and thereafter coat the microcapsules with a finely divided powder by means of a moving fluid bed. Suitable methods and apparatus are disclosed in U.S. Patent Nos. 2,986,475, 2,768,095 and 2,799,241. The substances employed to re-coat the microcapsules include commonly known encapsulating materials such as cellulose and synthetic polymers, including polyethylene, polypropylene, polymethylmethacrylate, polymethacrylate, etc.

As is apparent, substances such as inks, dyes, paints, adhesives, activated monomers, drug preparations, etc. can be encapsulated according to the instant invention. It is only necessary to apply reasonable care in order that the substances to be encapsulated do not interfere with the interfacial polycondensation of the particular reactants. By judicious selection, substantially any substance can be encapsulated. Thus, a substance to be encapsulated which will influence the interfacial polycondensation reaction of one pair of reactants is not likely to influence the polycondensation reaction of a second pair of reactants having substantially opposed character-

istics. As will be more fully apparent from the examples, polymer shells can be formed which are polyamides, polyurethanes, polysulfonamides, polyesters, polyureas, etc.

The following examples will serve to further illustrate the invention. However, it should be understood that the invention is not intended to be limited thereby. In the examples, proportions expressed are parts by weight unless otherwise indicated.

EXAMPLE 1

A volatile non-polar liquid encapsulated in a polyamide shell was prepared as follows: 4 parts polyvinyl alcohol and 0.1 part tetrasodium pyrophosphate were dissolved in 250 parts water. Thereafter, 25 parts terephthaloyl chloride in 67 parts toluene were emulsified in the aqueous medium, employing rapid agitation at a temperature of ca. 25° C.

A solution of 8 parts ethylenediamine, 0.5 part 1,6-hexanediamine, 10 parts sodium hydroxide and 75 parts water was made up and slowly added to the emulsion of terephthaloyl chloride and toluene with rapid agitation while maintaining the temperature at approximately 25° C. Substantially immediately upon addition of the amine solution, microscopic capsules were formed. When all the diamine solution had been added, the capsules were filtered and examined microscopically. Under pressure of a stylus, the capsule shells were ruptured to release the enclosed toluene.

EXAMPLE 2

A non-volatile liquid was encapsulated in a polyamide shell as follows: A solution of 10 parts of toluene, 87 parts methyl phthalyl ethyl glycolate and 25 parts of terephthaloyl chloride was emulsified into 250 parts water containing 0.1 part tetrasodium pyrophosphate and 4 parts polyvinyl alcohol with rapid agitation at approximately room temperature. To the above solution was slowly added a solution of 8 parts ethylenediamine, 0.5 part 1,6-hexanediamine and 10 parts sodium hydroxide in 75 grams water. Substantially immediately upon addition of the amine solution capsules were formed at the interface of the dispersed materials. The resultant capsules, upon crushing, exuded the enclosed methyl phthalyl ethyl glycolate.

EXAMPLE 3

A reactive constituent in a non-volatile liquid phase can be encapsulated in a polyamide shell as follows: 2 parts dichlorobenzoic acid, 25 parts terephthaloyl chloride, 10 parts toluene and 87 parts methyl phthalyl ethyl glycolate were emulsified into 250 parts water containing 4 parts polyvinyl alcohol and 0.1 part tetrasodium pyrophosphate by rapid agitation, maintaining the temperature at approximately 25° C. To the emulsion a solution of 16 parts ethylenediamine and 1 part 1,6-hexanediamine in 75 parts water was slowly added. Substantially immediately upon addition of the diamine solution, polymer formation occurred at the interface of the dispersed phase of the emulsion, forming microscopic capsules. On applying pressure to the microscopic capsules obtained, the oily fluid containing the dissolved dichlorobenzoic acid was exuded.

EXAMPLE 4

A non-volatile liquid was encapsulated in a polyester shell as follows: A solution of 15.5 parts terephthaloyl chloride in 10 parts toluene and 87 parts methylphthalyl ethyl glycolate was emulsified into 200 parts water containing 4 parts polyvinyl alcohol and 0.1 part tetrasodium pyrophosphate, employing rapid agitation while maintaining the temperature at approximately 25° C. To this emulsion was slowly added a solution of 17.5 parts 2,2-bis(4-hydroxyphenyl)propane and 6.2 parts sodium hydroxide in 100 parts water. Substantially immediately upon addition of the dissolved phenol polymerization occurred at the interface of the dispersed phase of the emulsion forming capsules which contained the methyl phthalyl ethyl glycolate as the liquid phase.

EXAMPLE 5

A continuous bond sheet having a film of microscopic capsules containing an inflammable liquid on one surface was prepared as follows: 5 parts terephthaloyl chloride and 150 parts petroleum solvent having a boiling point of 194–205° F., a flash point of 25° F., and a specific gravity of 0.741 at 60° F. and 95% of which distilled in the temperature range of 235–247° F, was emulsified in 350 grams of a 2% aqueous gum-arabic solution utilizing high speed agitation in a Waring Blendor and ambient temperature. The emulsion was immediately added to a solution of 10 parts diethylenetriamine in 150 parts of water and the mixture stirred vigorously by hand. A film of microcapsules having a wet thickness of 0.003 inch was drawn down on a continuous bond sheet and oven dried at 95° C. On applying pressure to the surface of the coating to rupture the shell of the microcapsule, copious amounts of the enclosed liquid were exuded. In order to determine the nature of the encapsulated liquid, a flint spark was applied to the unruptured coating and no ignition took place. After rupture of the coating, however, and exudation of the liquid, immediate ignition took place on sparking indicating that the liquid was the flammable petroleum solvent. The film of microcapsules was oven heated at 95° C. for 48 hours and re-tested. No apparent change occurred in the nature or amount of encapsulated liquid.

EXAMPLE 6

An activated monomer encapsulated in a polyamide shell was prepared as follows: 3.75 parts terephthaloyl chloride, 0.5 part azodiisobutyronitrile and 100 parts methyl methacrylate were emulsified in 180 parts water containing 4.5 parts polyvinyl alcohol by rapid agitation at approximately 25° C. The emulsion was thereafter poured into a solution of 1.25 parts diethylene triamine and 1.5 parts sodium hydroxide in 180 parts water and the mixture was allowed to stand for several minutes. The microcapsules formed were examined microscopically and under applied pressure the capsules were observed to rupture and exude the methyl methacrylate. A thin sample of these microcapsules on a microscopic slide was subjected to ultraviolet irradiation for 30 minutes and re-examined. No exudation took place under pressure indicating that the enclosed liquid monomer had been converted to the solid polymer by ultraviolet activated addition polymerization.

EXAMPLE 7

Microcapsules containing water in a polyamide shell were prepared as follows: 2 parts terephthaloyl chloride were dissolved in 100 parts mineral spirits. A second solution of 5 parts diethylenetriamine dissolved in 200 parts water was prepared. A glass tube was heated and drawn out to provide a fine orifice having an opening of approximately 0.1 millimeter in diameter. 5 parts of the aqueous triamine solution was extruded through the orifice under high pressure into the acid chloride solution. Small droplets were formed in the acid chloride solution which substantially instantaneously became encased in a polymer shell formed at the interface. The capsules were collected and examined and were found to contain water.

EXAMPLE 8

Glycerine was encapsulated in a polyamide shell as follows: 2 parts terephthaloyl chloride was dissolved in 100 parts mineral spirits. A second solution was prepared containing 5 parts diethylenetriamine and 200 parts glycerine. A glass tube was heated and drawn out to give a fine orifice having an opening of 0.1 millimeter in diameter. 5 parts of the triamine solution was extruded through the orifice under pressure into the acid chloride

solution. Small droplets were dispersed in the acid chloride solution and substantially instantaneously became encased by the polymer formed at the interface. The capsules were collected and examined and were found to contain glycerine.

EXAMPLE 9

A polyglycol having an average molecular weight of 400 was encapsulated in a polyamide shell, employing the procedure described in Example 8. The capsules, when examined, were found to contain the polyglycol.

EXAMPLE 10

Concentric multi-wall capsules, each wall separated by a layer of liquid, were prepared as follows: A solution containing 2 parts terephthaloyl chloride in 100 parts mineral spirits was prepared. A second solution containing 5 parts diethylenetriamine in 200 parts water was made up. Relatively large drops (1–10 mm.) of the diacid chloride solution were introduced into the triamine solution and allowed to stand therein for 2 minutes during which time a polymer shell formed around each drop. These capsules were carefully removed, allowed to drain, then immersed in the diacid chloride solution. A second interfacial film of the same polymer formed around the original capsule but was separated from the original shell by a thin layer of aqueous triamine solution. these double walled capsules were carefully removed, drained and reimmersed in the aqueous triamine solution to form a third film of polymer separated from the second film by a thin layer of mineral spirits solvent. Alternate dipping was continued until six distinct concentric shells, each separated alternately by aqueous and mineral spirits solvent layers, were formed about the original drop.

EXAMPLE 11

A dispersion of previously formed microcapsules can be encapsuleted as follows: 3.75 parts terephthaloyl chloride, 0.5 part azodiisobutyronitrile and 100 parts of methyl methacrylate were emulsified in 180 parts water containing 4.5 parts polyvinyl alcohol. The emulsion was then poured into a solution of 1.25 parts diethylenetriamine and 1.5 parts sodium hydroxide in 180 parts of water and the mixture allowed to stand for several minutes. Microcapsules containing liquid methyl methacrylate encased in a polyamide shell were obtained.

10 parts of the dispersed microcapsules containing monomer were injected under pressure into a solution of 5 parts terephthaloyl chloride in 200 parts toluene. The injected stream broke up into droplets of the triamine dispersion and a polymer film formed instantaneously at the interface of the droplets, thereby effectively encapsulating the dispersion of the previously formed microcapsules.

EXAMPLE 12

A volatile organic liquid is encapsulated in a polyamide shell and thereafter re-coated as follows: A solution of hexamethylenediamine was prepared by dissolving 9.28 parts hexamethylenediamine and 6.4 parts sodium hydroxide in 200 parts water. A 0.4 molar solution of sebacoyl chloride was made up by dissolving 1.47 parts sebacoyl chloride in carbon tetrachloride. Thereafter, 0.5 part polyvinyl alcohol was dissolved in 100 parts water and 50 parts of the solution were added to 10 parts of the 0.4 molar solution of sebacoyl chloride in carbon tetrachloride, prepared as above, providing a coarse suspension of carbon tetrachloride in water. To this suspension was added 10 parts of the aqueous diamine solution with gentle stirring. A dispersion of capsules was formed, each capsule having carbon tetrachloride encased in a polyamide shell. Excess diamine was removed by decantation and the capsules washed several times in tap water. 50 grams of a 2% aqueous polyvinyl alcohol solution was added to the capsules and the dispersion spray dried to give a secondary coating of polyvinyl alcohol about each capsule.

In the above examples in which the polycondensate is a polyamide, the amine can be replaced with other amines including 2,5-dimethyl piperazine, propylenediamine, triethylenetetraamine, tetramethylenediamine and piperazine. The terephthaloyl chloride can be replaced by other compounds including orthophthaloyl chloride.

In Example 4, the 2,2-bis(4-hydroxyphenyl)propane can be replaced by other hydroxy compounds including 4,4'-dihydroxybiphenyl, 1,2-bis(4-hydroxyphenyl)ethane; 2,2-bis(4-hydroxyphenyl)butane; 3,3-bis(4-hydroxyphenyl)pentane; 2,2-bis(4-hydroxyphenyl)pentane; 4,4'-dihydroxydiphenyl sulfone and 4,4'-dihydroxybenzophenone. The terephthaloyl chloride can be replaced by other diacid chlorides including isophthaloyl chloride, bis(4-chlorocarbonylphenyl)ether and phosgene.

In Examples 1–12, the polyamide and polyester condensates can be replaced by other condensates including polyurea condensates of phosgene and hexamethylenediamine, polyurethane condensates of tetramethylene bischloroformate and tetramethylenediamine; ethylene bischloroformate and piperazine and sulfonamides of 1,3-benzenedisulfonyl chloride and hexamethylene diamine. Thus, substantially any pair of reactants can be employed which will undergo interfacial polycondensation. Furthermore, the ratio of the reactants which take place in the interfacial polycondensation can vary over a relatively wide range. Thus, either reactant can be employed in a large excess. However, it is preferred that substantially stoichiometric amounts be selected. Additionally, the polycondensation reaction will occur over a broad temperature range. It has been found that the encapsulation process can be carried out advantageously at ambient temperatures, as well as temperatures approaching the boiling point of the continuous or dispersed phase. The proper selection of temperatures and proportions is within the ability of one skilled in the art having the instant specification, particularly the examples, as a guide. By judiciously selecting the particular reactants in relation to the substances to be encapsulated, the desirable characteristics of the polycondensate film can be advantageously employed. In many respects, insolable, infusible condensation polymers are superior to addition-type polymers.

The capsules formed according to the instant invention can have diameters which vary quite widely depending to a substantial extent upon the nature of the dispersion. Thus, if the globules of the dispersion are extremely fine, the diameter of the capsules will be extremely small. However, if the dispersion is relatively coarse, the capsules will increase in diameter. Capsules having diameters of from about 0.1 micron to about 0.3 inch can be obtained. The thickness of a single encapsulating shell can vary from about 0.1 micron to about 450 microns. The total thickness of a multiwall capsule shell can be several times greater.

As noted hereinbefore, the internal phase of a single capsule or an intermediate layer between shells of a multiwall capsule may consist of solid, liquid or gas or any heterogeneous or homogeneous combination of the above. Furthermore, it may be desirable that the internal phase have a particular state during encapsulation, but is converted to a second state after completion of the encapsulation process, i.e., a liquid monomer converted to a polymer. The nature of a material during encapsulation may also be completely changed by suitable treatment after completion of encapsulation.

It should be appreciated that while there are above disclosed but a limited number of embodiments of this invention, it is possible to produce still other embodiments without departing from the inventive concept set forth.

It is claimed and desired to secure by Letters Patent:

1. The method of encapsulating a substance in a shell of solid synthetic condensation polymer formed by the

polycondensation of two polyfunctional reactants adapted to condense to give said polymer, which method comprises the steps of: (1) dispersing one of said reactants and said substance to be encapsulated in the first fluid continuous phase, (2) dissolving said second reactant in a second fluid continuous phase which is a solvent for said second reactant and which is compatible with said first continuous phase, and (3) admixing said two continuous phases, whereby the reactants therein condense to form microcapsules of said substance in a shell of said polymer.

2. The process of claim 1, wherein the continuous phases of said step (1) and of said step (2) are each water.

3. The process of claim 1, wherein an emulsifying agent is employed in forming dispersion of said step (1).

4. The method of encapsulating a substance in a shell of solid synthetic condensation polymer formed by the polycondensation of two polyfunctional reactants adapted to condense to give said polymer, which method comprises the steps of: (1) forming a solution of one of said reactants and said substance, (2) dissolving the other of said reactants in a liquid solvent which is immiscible with said solution of step (1), and introducing said solution from step (1) as droplets into the solution of step (2), whereby the reactants therein condense to form microcapsules of said substance in a shell of said polymer.

5. The process of claim 4, wherein solution (1) is passed into solution (2) by passing said substance through an orifice under pressure.

6. The process of claim 4 wherein the solution of step (1) is formed by dissolving said first reactant in a liquid substance which is a solvent for said first reactant.

7. The process of claim 6 wherein the solution of step (1) is formed by dissolving said first reactant and said substance in a liquid which is a solvent for both said first reactant and said substance.

References Cited

UNITED STATES PATENTS

3,078,242	2/1963	Morgan	18—54 X
3,208,951	9/1965	Berger et al.	252—316

RICHARD D. LOVERING, *Primary Examiner.*

U.S. Cl X.R.

44—7; 106—19; 117—100; 167—83; 252—188.3; 260—29.1, 89.5; 264—4

EXHIBIT F
Downie 61

Q. That would be the reason that someone else wouldn't put the request to you. That sounds a little speculative to me. The reason I asked that question - -

A. Well, I would hope that they wouldn't wait around until I got back, they would feel free to go direct to Dr. Macaulay because he has the responsibility and the authority to act in this area.

Q. All right. Now, are those - - I am sorry, what is the title of those reports again, Annual Research Reports?

A. Yes.

Q. And are they bound volumes or - -

A. No, spiral volumes.

Q. Yes and how are the reports broken down as to projects or topic?

A. In the broad department areas that we spoke about, research, mechanical research, I should say, technical service, process research and electronic breakdown and then we have individual project titles under those.

Q. Do you know what the title is that the project we have been referring to as the MCP Project carries?

A. It would be Moore Carbonless Paper or Encapsulation Processes.

Q. During this period where you were concerned with the large scale production of MCP, which of the various sections of the Research Department address themselves to that problem?

A. Chemical and the Process Engineering, Joe Yeh.

Q. Did you ever see any of these capsules that were made in your - - by your Chemical Section Group?

A. Only some spillage up in Green Bay, that is all.

Q. Did you ever see any here in the form of a free flowing powder?

A. No. I very rarely go out in the lab.

Q. And by "spillage", I assume you mean the - -

A. Slurring.

Q. The slurring of capsules that - -

A. Yes. That is the only thing I remember seeing.

Q. You haven't seen them in powder form?

A. No.

MR. DELAHUNT: I have no further questions.

MR. AMES: No questions.

(Deposition terminated.)

IN THE UNITED STATES DISTRICT COURT
FOR THE WESTERN DISTRICT OF NEW YORK

MOORE BUSINESS FORMS, INC., Plaintiff, v. MINNESOTA MINING AND MANUFACTURING COMPANY, Defendant.	)	Civil Action No. CIV 1972-47

AFFIDAVIT OF DEAN A. OSTLIE
IN SUPPORT OF DEFENDANT'S
MOTION FOR SUMMARY JUDGMENT

STATE OF MINNESOTA)
) ss.
COUNTY OF RAMSEY)

DEAN A. OSTLIE, being first duly sworn, deposes and states as follows:

1. I am presently employed by the defendant, Minnesota Mining and Manufacturing Company (3M), as Research Manager in its Paper Products Division. I have held this position since about September, 1966, and from 1962 until September, 1966, held the position of Senior Research Chemist in the same division.

2. I received a Bachelor's Degree in Chemistry from St. Olaf College, Minnesota, in 1953, and a Degree of Doctor of Philosophy in Organic Chemistry from the University of Minnesota, conferred in 1957.

3. I am, and since prior to the year 1966 going back to their inception have been, thoroughly familiar with all commercial products containing microcapsules manufactured by the Paper Products Division of 3M.

4. 3M, through its Paper Products Division, manufactures and markets carbonless paper products, presently designated "3M" brand carbonless paper Type 100, and "3M" brand carbonless

paper Type 200. Each of these products contains coated on the surface thereof (Type 200), or within the paper matrix itself (Type 100) microscopic capsules containing an imaging fluid. When these sheets are impacted, for example, by a writing instrument, typewriter key, etc., capsules are ruptured in the impacted areas, releasing fluid which reacts with other components to form an image in the impacted area.

5. In the case of Type 100 carbonless paper, the other component with which the imaging fluid released from the capsules reacts is also contained within the paper matrix. Thus, the Type 100 paper can be imaged by itself without the presence of any other sheet or companion structure simply upon impact. This product is thus referred to as a self-imaging or self-contained carbonless paper.

6. Type 200 carbonless paper is designed to be used where two or more sheets are employed in superposition. In the Type 200 system, the microcapsules containing the imaging fluid are coated on the back surface of a sheet and the component with which the fluid reacts upon release through impacting of the capsules is contained on the front surface of the underlying sheet so that then the two sheets are together and impact occurs, an image is formed on such underlying sheet.

7. The capsule layer in the Type 200 paper contains, in addition to the just-mentioned imaging microcapsules, a small quantity of relatively larger "scuff" microcapsules. The scuff capsules serve simply as spacers to minimize intimate contact between adjoining sheets or plys in the Type 200 system, the purpose being to avoid premature or inadvertent discoloration.

8. The only carbonless papers containing microcapsules which are or ever have been manufactured by 3M have been manu-

factured by the Paper Products Division of 3M. The Type 100 paper, although prior to mid-1966 marketed under a different brand name, viz., "Action" paper, has been manufactured and marketed continuously since 1962; and the Type 200 paper has been marketed since 1967.

9. Three, and three only, classifications or types of microcapsules are and have been employed by 3M in the manufacture of its carbonless papers, namely, the imaging capsules employed in "3M" brand carbonless paper Type 100, and the imaging capsules and the larger "scuff" capsules employed in "3M" brand carbonless paper Type 200.

10. In my deposition which was taken on behalf of plaintiff in this action on June 8, 1973, I was interrogated in respect to the manufacture of each of the three classes of capsules employed in my company's carbonless papers, as well as the manner in which those capsules were incorporated into the carbonless paper products.

11. Attached hereto as Exhibit A is a copy of plaintiff's Ostlie Dep. Exhibit 10 for indentification marked during my said deposition, this document being a copy of two columns from my company's Patent No. 3,516,941 with certain handwritten amendments entered thereon in my handwriting. The printed text of said exhibit describes the manufacture of microcapsules employed in "3M" brand carbonless paper Type 100 in or about 1966. The handwritten amendments on Exhibit A (Ostlie Dep. Exh. 10) conform the ingredients, amounts of ingredients and procedures to the capsule manufacturing process employed by 3M from and after December 28, 1970.

12. Attached hereto as Exhibit B is a copy of plaintiff's Ostlie Dep. Exhibit 12, as identified in my aforesaid deposition taken June 8, 1973. Said exhibit is a copy of the same printed portion of 3M Patent No. 3,516,941 referred to in paragraph 11

above, but on which I made handwritten amendments to conform the description therein to that of the manufacture of commercial imaging microcapsules as used in "3M" brand carbonless paper Type 200 from and after March 22, 1973.

13. Attached hereto as Exhibit C is a copy of plaintiff's Ostlie Dep. Exhibit 14, as identified in my aforesaid deposition taken June 8, 1973. Said exhibit is a copy of the same printed portion of 3M Patent No. 3,516,941 as referred to in paragraphs 11 and 12 above, but on which I made handwritten amendments to conform the description therein to that of the manufacture of commercial scuff microcapsules as used in "3M" brand carbonless paper Type 200 from and after November 16, 1971.

14. As can be seen from Exhibits A-C (plaintiff's Ostlie Dep. Exhs. 10, 12 and 14, respectively), all of the microcapsules therein described as employed in 3M's commercial carbonless papers are formed in an aqueous slurry, which slurry is of a pumpable consistency and contains more than one-half water. This has always been the case. While over the years there have been some slight changes in ingredients, amounts of ingredients and process conditions, at no time since the inception of 3M's carbonless paper products have these differences led to the formation of microcapsules other than in an aqueous slurry of pumpable consistency containing more than one-half water.

15. Following manufacture for incorporation into the commercial Type 100 carbonless papers as above described, the aqueous slurry of capsules is dumped or pumped into a paper-making machine where it is blended with paper fibers and other ingredients in the paper-making operation.

16. Following manufacture for coating in Type 200 carbonless paper as above described, the aqueous slurry of imaging capsules is pumped or dumped into a tank where blending occurs with the aqueous slurry of scuff capsules as well as with other ingredients, and this aqueous solution is then coated onto paper in the formation of the microcapsules-containing coating of the Type 200 paper.

17. Inasmuch as the equipment on which the final carbonless paper product is made is located at a different place - and frequently at a different plant site - than the site of manufacture of the microcapsule slurry, it is necessary to transport the microcapsules from the site of microcapsule manufacture to the site of final product formation. In these operations, the microcapsules are handled as a slurry always containing more than one-half water. This has been true of 3M's manufacture of all of its commercial carbonless papers since their inception.

18. At no point from the formation of microcapsules to the production and packaging of the carbonless paper products, can the microcapsules employed in any carbonless product of 3M be characterized as a "free flowing powder". The microcapsules employed in 3M carbonless papers Type 100 and Type 200 (including as sold under the prior brand name "Action") are not produced in a process for producing a free flowing powder, and are never reduced in form to a free flowing powder. Neither have the said carbonless paper products employing such capsules been formed from or with a free flowing powder of microscopic discrete rupturable capsules.

Further affiant sayeth not.

Dean A. Ostlie

Dean A. Ostlie

Subscribed and sworn to before
me this 29th day of June, 1973.

Ruth E. Johnson

Notary Public

RUTH E. JOHNSON
NOTARY PUBLIC-MINNESOTA
RAMSEY COUNTY
My Commission Expires May 3, 1980

T-100 12-28-70 →

EXHIBIT A

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imaging or marking papers was carried out as follows:

The capsule fill was composed of:

Material	Lbs./100
Charge:	
A..... Cyclohexane	64.6
B..... Dibutyl phthalate	15.7
C..... Tributyl phosphate	14.2
D..... N,N'-bis(2-ethylhexyl)-dithiooxamide	4.0
E..... N,N'-bis(dicosyl)-dithiooxamide	1.5

The materials are mixed in the order of their recitation above in a stainless steel kettle equipped with an agitator and heating jacket at about 100° F., charge A being first added, and the remainder of the charges being added thereafter. After the temperature of the batch reaches 100° F., continue agitation at this temperature for one hour.

The precondensate solution is composed of:

	Material	Lbs./100
Charge:		
A..... 32.44	Formalin	24.8
B.....	Triethanolamine	1.5
C..... 13.21	Urea	11.10
D..... 53.21	Soft water	50.25
E.....	Salt (NaCl)	8.25

The formalin is 37–38% formaldehyde and is stabilized with 7% methanol. The formalin is first added to a large stainless steel kettle equipped with an agitator and heating jacket and the temperature control set at [illegible] F. then charges B and C are added in the order recited with continued agitation. After the batch reaches 160° F. it is reacted with continued agitation for 2½ hours, then the temperature control is reduced to [illegible] F. Next charges D and E are added and the precondensate solution is ready for use. The concentration (exclusive of charge E) is about 24% solids.

The precondensate solution and the fill are combined to make capsules in a 300 gallon kettle as follows:

Ingredient	Lbs./100	Total lbs. in batch
Charge:		
A..... Precondensate solution	75.22	2132.9
B..... Hydrochloric acid (12% 6)	[illegible]	[illegible]
C..... Fill	97.11	2752.0
D..... Hydrochloric acid (12.5%)	[illegible]	[illegible]
E..... Hydrochloric acid (12.5%)	[illegible]	[illegible]
F..... Caustic (5% NaOH)	[illegible]	[illegible]
Cold water	[illegible]	[illegible]

The precondensate solution, charge A, is pumped into a stainless steel kettle equipped with heating jacket and a high shear agitator with a 10" turbine. The temperature is from 65° F. to 95° F. Charge B is added to neutralize the solution while the temperature of the solution is within about 2° of the selected temperature in the 65–95° F. range, charge C is added and agitator speed adjusted to about 1150 r.p.m. Five minutes after agitator speed adjustment, charge D is added over a five minute period and then after a wait of 12 minutes, charge E is added over a 12 minute period to provide the dispersions with a pH of 2.3 ± .3. One hour after the addition of charge E, set temperature control to 140° F., and three hours after charge E addition, add charge F and pump the neutralized slurry into a storage tank for subsequent use. The resultant capsules have an average particle size in the range of 12 to 20 microns.

To test the capsules for the requisite strength and permeability a group of four handsheets of paper is made. 635 ml. of bleached sulfite pulp (e.g. Ponderosa with a 90 brightness value) at 1.57% solids and 30° S.R. (Schopper-Riegler) is diluted with 1365 ml. soft water in preparation for making test hand sheets. To this aqueous slurry is added in succession (1) 6 ml. of capsule slurry (24% capsules), (2) 4 ml. of 10% $NiCO_3 \cdot 6H_2O$ and (3) 8 ml. of 10% "Dresinate X" (sodium rosinate from Hercules Co.). A mix time of 2 minutes is used between each addition. (Dry parts=100–15–4–8). The nickel sulfate reacts with the sodium rosinate to form nickel rosinate, which is a co-reactant for the capsule containing dye precursor; upon reaction of these components, a bright deep blue to purple permanent image is formed.

400 ml. of the above slurry is diluted to 3300 ml. in a William's 3 x 8 in. handsheet mold and the sheet formed on a 100 mesh wire. The sheet is couched from the wire onto blotter stock and then is pressed between dry blotters at 50 p.s.i. for 5 minutes. The blotters are removed and the sheet is dried on a polished hot-can drier at 220° F. until dry (approximately 10 minutes).

This yields a handsheet of about 50 lbs. basis weight (3000 sq. ft. ream size). The sheet can be readily marked by machine key impact or stylus pressure which ruptures capsules and releases the contents for reaction with the nickel rosinate.

The sheets are tested by reading the background brightness of a stack of 4 sheets, to make sure that the reading is of the paper and is not influenced by the background of the surface on which the paper rests, with a "Photovolt" Reflection Meter equipped with a green filter, Model 610, marketed by Photovolt Corp. New York, N.Y. A value of 76% reflected light is the minimum acceptable value for use of the capsules in a paper furnish for making self-contained impact paper on a paper machine, which paper can be dried, wound, slit and stacked without undue smudging or adventitious marking. A value lower than 76% reflectance indicates weak or permeable capsules which has led to premature coloration of the handsheet by completing of the dithiooxamide derivatives in the capsule fill, i.e., the dye precursor, with the nickel rosinate formed from the reaction of the nickel sulfate with the "Dresinate X." Urea-formaldehyde capsules made by the procedure of Matsukawa Pat. No. 3,914,303 resulted in grossly discolored sheets.

Using substantially the same fill, precondensate and other materials as in the charges noted in the previous part of this example, but varying the pH of the polymerization, and running the polymerization in these varying pH ranges, with and without sodium chloride addition, capsules were made over a polymerization period of about 16 hours (because of the higher pH range, longer polymerization times are required). Handsheets of self-contained impact paper containing such capsules were then made as previously described in this example and the following results were obtained with the meter reflectance tests.

Grms. of salt added to each 100 grms. of precondensate	pH	Polymerization cure temperature, °C.	Percent reflectance
0	4.5	44	79
8	5.0	54	79
10	4.8	58	78
10	5.0	56	63

It will be noted that with the salt addition capsules tough enough to withstand the rigors of the handsheet reflectance test for self-contained impact paper resulted even at a pH as high as 5, whereas with no salt addition to the precondensate, the resulting capsules yielded paper having reflectance values below the minimum acceptable reflectance for useful self-contained impact papers. Polymerization at a pH of 5.5 resulted in incomplete encapsulation of the fill material. It should be noted that even at a reflectance reading of 78, the paper has a decidedly blue cast to it, whereas at 63 the paper is quite discolored throughout.

EXAMPLE 19

A manifolding paper utilizing the capsules of the invention was made as follows:

A prepolymer was prepared as in Example 18, except

ONLY COPY AVAILABLE

T-200 (3-22-73)

EXHIBIT B

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imaging or marking papers was carried out as follows:

The capsule fill was composed of:

Material		Lbs./100	
Charge:			
A	Cyclohexane	62.6	64.8
B	Diethyl phthalate	15.7	15.7
C	Tributyl phosphate	14.2	14.3
D	N,N'-bis(2-ethylhexyl)-dithiooxamide	4.0	4.9
E	N,N'-bis(formyl)-dithiooxamide	1.5	1.3

The materials are mixed in the order of their recitation above in a stainless steel kettle equipped with an agitator and heating jacket at about 100° F., charge A being first added, and the remainder of the charges being added thereafter. After the temperature of the batch reaches 100° F., continue agitation at this temperature for one hour.

The precondensate solution is composed of:

Material		Lbs./100	
Charge:			
A	Formalin	32.44	22.8
B	Triethanolamine	1.16	.15
C	Urea	15.62	11.10
D	Soft water	50.78	60.20
E	Salt (NaCl)	1.00	9.22

The formalin is 37–38% formaldehyde and is stabilized with 7% methanol. The formalin is first added to a large stainless steel kettle equipped with an agitator and heating jacket and the temperature control set at 167° F. then charges B and C are added in the order recited with continued agitation. After the batch reaches 160° F. it is reacted with continued agitation for 2½ hours, then the temperature control is reduced to 75° F. Next charges D and E are added and the precondensate solution is ready for use. The concentration (exclusive of charge E) is about 24% solids.

The precondensate solution and the fill are combined to make capsules in a 300 gallon kettle as follows:

Ingredient		Lbs./100	Total lbs. in kettle
Charge:			
A	Precondensate solution	57.67	135
B	Hydrochloric acid (12.5%)	.17	.5
C	Water	29.07	68.0
D	Hydrochloric acid (12.5%)	.21	.5
E	Hydrochloric acid (12.5%)	.24	.5
F	Caustic (5% solution)	.49	3.4
G	Soft water	12.15	28.6

NaCl 3.64 — NH4OH (30%) 3.27 — 23.8

The precondensate solution, charge A, is pumped into a stainless steel kettle equipped with heating jacket and a high shear agitator with a 10" turbine. The temperature is from 65° F. to 95° F. Charge B is added to neutralize the solution. When the temperature of the solution is within about 2° of the selected temperature in the 65–95° F. range, charge C is added and agitator speed adjusted to about 1150 r.p.m. Five minutes after agitator speed adjustment, charge D is added over a five minute period and then after a wait of 12 minutes, charge E is added over a 12 minute period to provide the dispersions with a pH of 4.2±.3. One hour after the addition of charge E, set temperature control to 140° F., and three hours after charge E addition, add charge F and pump the neutralized slurry into a storage tank for subsequent use. Charge G is added to rinse the kettle and is pumped to the storage tank. The resultant capsules have an average particle size in the range of 12 to 20 microns.

NaCl added & dissolved — 1.9±.3 — 24 — 8-15

To test the capsules for the manufacture of self-contained impact papers, a group of four handsheets of paper is made. 635 ml. of bleached sulfite pulp (e.g. Canpeco with a 90 brightness value) at 1.37% solids and 580° SR (Schopper-Riegler) is diluted with 1365 ml. soft water in preparation for making test handsheets. To this aqueous slurry is added in succession (1) 6 ml. of capsule slurry (25% capsules), (2) 4 ml. of 10% $NaSO_4$ solution and (3) 8 ml. of 10% "Dresinate X" (sodium rosinate from Hercules Co.). A mix time of 2 minutes is used between each addition. (Dry parts=100–15–4–8). The nickel sulfate reacts with the sodium rosinate to form nickel rosinate, which is a co-reactant for the capsule containing dye precursor; upon reaction of these components, a bright deep blue to purple permanent image is formed.

400 ml. of the above slurry is diluted to 3300 ml in a William's 8 x 8 in. handsheet mold and the sheet formed on a 100 mesh wire. The sheet is couched from the wire onto blotter stock and then is pressed between dry blotters at 50 p.s.i. for 5 minutes. The blotters are removed and the sheet is dried on a polished hot-can dryer at 220° F. until dry (approximately 10 minutes).

This yields a handsheet of about 30 lbs. basis weight (3000 sq. ft. ream size). The sheet can be readily marked by machine key impact or stylus pressure which ruptures capsules and releases the contents for reaction with the nickel rosinate.

The sheets are tested by reading the background brightness of a stack of 4 sheets, to make sure that the reading is of the paper and is not influenced by the background of the surface on which the paper rests, with a "Photovolt" Reflection Meter equipped with a green filter, Model 610, marketed by Photovolt Corp. New York, N.Y. A value of 76% reflected light is the minimum acceptable value for use of the capsules in a paper furnish for making self-contained impact paper on a paper machine, which paper can be dried, wound, slit and stacked without undue smudging or adventitious marking. A value lower than 76% reflectance indicates weak or permeable capsules which has led to premature coloration of the handsheet by complexing of the dithiooxamide derivatives in the capsule fill, i.e., the dye precursor, with the nickel rosinate formed from the reaction of the nickel sulfate with the "Dresinate X." Urea-formaldehyde capsules made by the procedure of Macaulay Pat. No. 3,016,303 resulted in grossly discolored sheets.

Using substantially the same fill, precondensate and other materials as in the charges noted in the previous part of this example, but varying the pH of the polymerization, and running the polymerization in these varying pH ranges, with and without sodium chloride addition, capsules were made over a polymerization period of about 16 hours (because of the higher pH range, longer polymerization times are required). Handsheets of self-contained impact paper containing such capsules were then made as previously described in this example and the following results were obtained with the meter reflectance tests.

Gms. of salt added to each 100 gms. of precondensate	pH	Polymerization temperature, °C.	Percent reflectance
0	4.5	55	79
0	5.0	55	79
10	4.5	55	73
10	5.0	55	63

It will be noted that with the salt addition capsules tough enough to withstand the rigors of the handsheet reflectance test for self-contained impact paper resulted even at a pH as high as 5, whereas with no salt addition to the precondensate, the resulting capsules yielded paper having reflectance values below the minimum acceptable reflectance for useful self-contained impact papers. Polymerization at a pH of 5.5 resulted in incomplete encapsulation of the fill material. It should be noted that even at a reflectance reading of 73, the paper has a decidedly blue cast to it, whereas at 63 the paper is quite discolored throughout.

EXAMPLE 19

A manifolding paper utilizing the capsules of this invention was made as follows:

A prepolymer was prepared as in Example 18, except

Scuff (11-16-71)

EXHIBIT 5

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imaging or marking papers was carried out as follows:

The capsule fill was composed of:

Material	Lbs./100
Charge:	
A..... Cyclohexanone..... 100	64.5
B..... Diethyl phthalate.....	15.7
C..... Triethanolamine.....	14.3
D..... N,N'-bis(2-hydroxyethyl) dithiooxamide..	4.0
E..... N,N'-bis(2-methoxyethyl)dithiooxamide....	1.5

The materials are mixed in the order of their recitation above in a stainless steel kettle equipped with an agitator and heating jacket at about 100° F., charge A being first added, and the remainder of the charges being added thereafter. After the temperature of the batch reaches 100° F., continue agitation at this temperature for one hour.

The precondensate solution is composed of:

	Material	Lbs./100
Charge:		
A..... 92.46	Formalin.....	22.9
B..... 1.71	Triethanolamine.....	.18
C..... 12.74	Urea.....	11.10
D..... 54.41	Soft water.....	60.20
E.....	Salt (NaCl).....	9.22

The formalin is 37–38% formaldehyde and is stabilized with 7% methanol. The formalin is first added to a large stainless steel kettle equipped with an agitator and heating jacket and the temperature control set at 160° F. then charges B and C are added in the order recited with continued agitation. After the batch reaches 160° F. it is reacted with continued agitation for 2½ hours, then the temperature control is reduced to 75° F. Next charges D and E are added and the precondensate solution is ready for use. The concentration (exclusive of charge E) is about 24% solids.

The precondensate solution and the fill are combined to make capsules in a 300 gallon kettle as follows:

Ingredient	Lbs./100	Total lbs. in Kettle
Charge:		
A..... Precondensate solution..... 42.50	31.90	135.5
B..... Hydrochloric acid (12.0%)..... 1.03	.13	5.4
C..... Fill..... 4.71	14.73	187.0
D..... Hydrochloric acid (12.0%)..... 1.79	.13	5.4
E..... Sodium chloride (25%).....	.20	8.0
F..... Ammonium hydroxide (30%).....	.13	5.8
G..... Water.....	.97	29.8

NH4OH (30%) 3.07 86

The precondensate solution, charge A, is pumped into a stainless steel kettle equipped with heating jacket and a high shear agitator with a 10" turbine. The temperature is from 65–85° F. Charge B is added to neutralize the solution. When the temperature of the solution is within about 2° of the selected temperature in the 65–85° F. range, charge C is added and agitator speed adjusted to about 1150 r.p.m. Five minutes after agitator speed adjustment, charge D is added over a five minute period and then after a wait of 10 minutes, charge E is added over a 10 minute period to provide the dye precursor with a pH of 2.2±.3. One hour after the addition of charge E, set temperature control to 140° F., and three hours after charge E addition, add charge F and pump the neutralized slurry into a storage tank for subsequent use. Charge G is added to rinse the kettle and is then pumped to the storage tank. The resultant capsules have an average particle size in the range of 15–30 microns.

To test the coated-back sheet-making and print-receiving ability a group of four handsheets of paper is made. 535 ml. of bleached sulfite pulp (e.g. Canpeco with a 90 brightness value) at 1.57% solids and 20° SR (Schopper-Riegler) is diluted with 1355 ml. soft water in preparation for making test handsheets. To this aqueous slurry is added in succession (1) 6 ml. of capsule slurry (25% capsules), (2) 3 ml. of 10% $NiSO_4 \cdot 6H_2O$ and (3) 3 ml. of 10% Dresinate X" (sodium rosinate from Hercules Co.). A mix time of 2 minutes is used between each addition. (Dry parts=100–15–4–8). The nickel sulfate reacts with the sodium rosinate to form nickel rosinate, which is a co-reactant for the capsule containing dye precursor; upon reaction of these components, a bright deep blue to purple permanent image is formed.

400 ml. of the above slurry is diluted to 3300 ml. in a William's 8 x 8 in. handsheet mold and the sheet formed on a 100 mesh wire. The sheet is couched from the wire onto blotter stock and then is pressed between dry blotters at 50 p.s.i. for 5 minutes. The blotters are removed and the sheet is dried on a polished hot-can drier at 220° F. until dry (approximately 10 minutes).

This yields a handsheet of about 30 lbs. basis weight (3000 sq. ft. ream size). The sheet can be readily marked by machine key impact or stylus pressure which ruptures capsules and releases the contents for reaction with the nickel rosinate.

The sheets are tested by reading the background brightness of a stack of 4 sheets, to make sure that the masking is of the paper and is not influenced by the background of the surface on which the paper rests, with a "Photovolt" Reflection Meter equipped with a green filter, Model 610, marketed by Photovolt Corp. New York, N.Y. A value of 76% reflected light is the minimum acceptable value for use of the capsules in a paper furnish for making self-contained impact paper on a paper machine, which paper can be dried, wound, slit and stacked without undue smudging or adventitious marking. A value lower than 76% reflectance indicates weak or permeable capsules which has led to premature coloration of the handsheet by complexing of the dithiooxamide derivatives in the capsule fill, i.e., the dye precursor, with the nickel rosinate formed from the reaction of the nickel sulfate with the "Dresinate X" Urea-formaldehyde capsules made by the procedure of Macaulay Pat. No. 3,016,303 resulted in grossly discolored sheets.

Using substantially the same fill, precondensate and other materials as in the charges noted in the previous part of this example, but varying the pH of the polymerization, and running the polymerization in these varying pH ranges, with and without sodium chloride addition, capsules were made over a polymerization period of about 16 hours (because of the higher pH range, longer polymerization times are required). Handsheets of self-contained impact paper containing such capsules were then made as previously described in this example and the following results were obtained with the meter reflectance tests:

Grms. of salt added to each 100 grms. of precondensate	pH	Polymerization cure temperature, °C.	Percent reflectance
0.....	4.5	55	79
0.....	5.0	55	79
10.....	4.5	55	73
10.....	5.0	55	63

It will be noted that with the salt addition capsules tough enough to withstand the rigors of the handsheet reflectance test for self-contained impact paper resulted even at a pH as high as 5, whereas with no salt addition to the precondensate, the resulting capsules yielded paper having reflectance values below the minimum acceptable reflectance for useful self-contained impact papers. Polymerization at a pH of 5.5 resulted in incomplete encapsulation of the fill material. It should be noted that even at a reflectance reading of 73, the paper has a decidedly blue cast to it, whereas at 63 the paper is quite discolored throughout.

EXAMPLE 19

A manifolding paper utilizing the capsules of the invention was made as follows:

A prepolymer was prepared as in Example 18, except

IN THE UNITED STATES DISTRICT COURT
FOR THE WESTERN DISTRICT OF NEW YORK

MOORE BUSINESS FORMS, INC., Plaintiff,	)	
v.	)	Civil Action
MINNESOTA MINING AND MANUFACTURING COMPANY, Defendant.	)	No. CIV 1972-47

MOTION OF DEFENDANT FOR
STAY OF DISCOVERY

PLEASE TAKE NOTICE that upon the Complaint, the Answer, the defendant's Motion for Summary Judgment, the annexed Affidavit of Stanley G. DeLaHunt, sworn to June 29, 1973, the annexed Affidavit of Waldo G. Bretson, sworn to June 29, 1973, and upon all the pleadings and proceedings heretofore had and taken herein, a Motion will be made at a motion term of this Court, to be held at the United States Courthouse, Buffalo, New York, on the 12th day of July, 1973, at 10:00 in the forenoon, or as soon thereafter as counsel can be heard, for an Order staying all further discovery in this action and all motions relating thereto until the hearing and determination of defendant's Motion for Summary Judgment dated July 2, 1973, on the grounds that a favorable decision on said Motion for Summary Judgment will make further discovery academic and moot.

Plaintiff, by motions for discovery pending in this Court, namely, Motion to Free Certain Documents from Stipulation of Non-Disclosure, and Motion Under Rule 37(a), F.R.Civ.P. for Order Compelling Answers to Interrogatories, by outstanding interrogatories, and by requests made during recent depositions taken by plaintiff, seeks much confidential information in respect

to the manufacture by 3M of microcapsules and products utilizing the same. Such information was developed by 3M at the cost of hundreds of thousands of dollars or more. Plaintiff, despite having spent 17 years in attempting to develop products such as it now accuses as an infringement, and despite the fact that the patent in suit was filed 16 years ago in August 1957 and issued a decade ago (January 9, 1962), announced its own carbonless paper product only as recently as April, 1972. Plaintiff is still having substantial quality problems with its product, and could only be aided by receipt of the information which it seeks unrestrictedly.

Quite apart from the dubious relevance of most of the information which plaintiff seeks, there is no need for plaintiff either to secure the information, or rulings in respect thereto, pending resolution of defendant 3M's companion Motion for Summary Judgment.

WHEREFORE, discovery in this case should be suspended pending determination of defendant's said Motion for Summary Judgment of Dismissal.

RAICHLE, BANNING, WEISS & HALPERN

By_____
A Member of the Firm

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IN THE UNITED STATES DISTRICT COURT
FOR THE WESTERN DISTRICT OF NEW YORK

MOORE BUSINESS FORMS, INC., Plaintiff,	)	Civil Action
v.	)	No. CIV 1972-47
MINNESOTA MINING AND MANUFACTURING COMPANY, Defendant.	)	

AFFIDAVIT OF STANLEY G. DELAHUNT
IN SUPPORT OF DEFENDANT'S
MOTION FOR STAY OF DISCOVERY

STATE OF MINNESOTA)
) ss
COUNTY OF RAMSEY)

STANLEY G. DELAHUNT, being first duly sworn, deposes and states as follows:

1. I am an attorney at law and of counsel for defendant in the above-captioned action.

2. Annexed hereto as Exhibit 1 are pages 47-48 of the deposition of plaintiff's employee, Dr. Norman Macauley, patentee of Macauley Patent No. 3,016,308 in suit, said deposition having been taken by defendant in this case on April 5-6, 1973.

3. Annexed hereto as Exhibit 2 are excerpts from defendant's Macauley Dep. Exh. 39, comprising excerpts of pages from various Annual Research Reports generated in the years 1961-69 in the Research Division of plaintiff Moore relating to Moore's carbonless paper development project.

4. Annexed hereto as Exhibit 3 is page 60 of the deposition of plaintiff's former Director of Research, Richard J. O'Brien, taken by defendant April 5, 1973.

5. Annexed hereto as Exhibit 4 is page 55 of the deposition of Robert H. Downie, plaintiff's Vice President and Director of Research, which deposition was taken by defendant April 4, 1973.

6. I attended the depositions taken by plaintiff of defendant's employees, Mr. Waldo G. Bretson, General Manager of the Paper Products Division of defendant, and Dr. Dean A. Ostlie, Research Manager of the said division, such depositions being taken by plaintiff June 6-8, 1973. During said depositions, requests were made by attorneys for plaintiff for, inter alia, the following:

(a) All records of the Chemolite City Pilot plant of defendant and the Graphic Systems Laboratory of defendant relating to the making of microcapsules.

(b) Representative documents of defendant covering the processes for making "3M" brand carbonless paper Type 100, microcapsules for such paper and processes for making such paper and such microcapsules for the last ten years.

(c) All documents of defendant, test results and materials relating to tests performed by defendant on "3M" brand carbonless paper Type 100 and any action taken by defendant on account thereof.

(d) All documents of defendant relating to microcapsules in any slurry for ten years.

(e) All documents relating to the manufacturing taking place in defendant's Nekoosa, Wisconsin manufacturing facility, and equipment contained therein.

(f) All patent disclosure forms of defendant written by Dr. Dean A. Ostlie, whatever the subject.

(g) All notebook pages and reports by Dr. Dean A. Ostlie and Dr. Timothy Jensen relating to the use of surfactants in microcapsule production.

Further affiant sayeth not.

Stanley G. DeLaHunt

Subscribed and sworn to before me this 29th day of June, 1973.

Ruth E Johnson

Notary Public

RUTH E. JOHNSON
NOTARY PUBLIC - MINNESOTA
RAMSEY COUNTY
My Commission Expires May 3, 1980

of developing a proprietary carbonless paper by August 6th, 1957?

A. I am not quite sure. I would have to check the records on that too.

Q. Within the scope of your definition.

A. Somewhere around that time I had succeeded in producing a paper of commercial quality. I would have to clarify the date.

Q. And was that proprietary carbonless paper of commercial quality one which included micro-capsules?

A. No.

Q. Is it your testimony, Dr. Macaulay, that somewhere along this time, you felt that you had attained the objective of coming up with a proprietary carbonless paper which did not have micro-capsules?

A. Yes.

Q. And did that work form the basis of one or more patent applications?

A. I am not quite sure.

Q. All right but can we agree that by August 6th, 1957, you had not attained your objective in

respect to a proprietary carbonless paper having or including micro-capsules?

A. Correct.

Q. Did the project continue on beyond August 6th, 1957?

A. Yes.

Q. And in pursuing the project, did you continue to endeavor to develop a proprietary carbonless paper which included micro-capsules?

A. Yes.

Q. And how long did that continue?

A. Up to the present date.

Q. And that has been a continuous project of yours throughout that time?

A. Well, it has been a continuous project of the company.

Q. Since prior to August 6th, 1957, is that correct, sir?

A. Yes.

Q. Now, you indicated that you were working alone on the project for some period of time, I believe from and after the date of Exhibit 18, December of 1955, is that correct?

EXCERPTS FROM ANNUAL RESEARCH REPORTS OF PLAINTIFF'S RESEARCH DIVISION

Report for 1961-62

4. Significant progress has been made in the development of microencapsulation techniques and we are closing the gap between laboratory specimens and production.

* * *

Report for 1963-64

2.2 The difficulty of obtaining sharp copies in manifold forms of more than 5 or 6 parts on high speed printers, and the cost and nuisance of removing and disposing of carbon sheets, has attracted much attention to the development of self contained manifold systems. NCR has been alone in this field for the past ten years and despite the handicap of high costs and relatively poor manifolding qualities has developed a substantial volume.

The recent introduction of 3M Action Paper, Kores Contact Paper, Oxford-Columbia Drion, The General Co. "Chemi-Sheet" and the Port Huron coated back paper are examples of this trend.

Our own development of a carbonless manifold system or a proprietorship in one of the most promising of the commercial systems we consider to be highly important.

* * *

Report for 1964-65

This project has top priority for 1965; approximately half the Chemical Development staff is assigned to it and we are prepared to transfer efforts from other projects if required.

Work on a self-contained copy paper has reached the final stage of laboratory development. It is planned to proceed with experimental machine coatings at International Paper in the first half of 1965.

* * *

Report for 1969

6. Colorless Dye Copying

As covered in Communications, we have achieved a breakthrough in our colorless dye program using high surface area clays which provide the basis for a superior, low-cost colorless copying system. These clays provide unusually intense, bright and extremely light stable colors with the preferred precursor of our copying system. Work during the year has also lead to the selection of a color precursor with all-round improved properties compared with the original precursor, and appreciably lower in cost. Work is proceeding to optimize the microencapsulation process, with a view to substantial cost reduction and no loss in product performance and quality. We are proceeding this year with a high priority program to have our product in volume production as early as possible.

chemist and I read them and they are incomprehensible to me so I can't answer that. I don't know what we are using really.

Q. The technology disclosed in the Macaulay Patent had been available at Moore for many years by 1963, had it not and I direct your attention to the fact that the Macaulay Patent was filed in 1957.

A. Right, right.

Q. Is it fair to say that as of 1963, the Macaulay disclosure had not led to any commercial product of Moore?

A. That is right. That is correct.

Q. And is it fair to say that as of 1970 when you retired, that the Macaulay Patent had not led to any commercial product of Moore?

A. Yes. We were getting ready but I don't think we had produced any commercial material at that time.

Q. You hadn't arrived yet.

A. Right.

Q. What was the nature of the Macaulay - - I am sorry, Dr. Macaulay's project in 1963? In connection

A. That would be this CFCB, period.
Q. The Type 200 paper of 3 M?
A. Right.
Q. Does Moore have a self-contained paper?
A. Not commercial.
Q. Are you working on one?
MR. AMES: If this is a trade secret - -
A. Among other things, yes.
Q. Have you gotten close enough to the bench work to appreciate that that is a more difficult product to make than the transfer type paper, the CFCB Type?
A. No.
Q. You couldn't help us on whether it is or isn't a more difficult one to make as a practical matter?
A. Well, you see, once again I have to put it against the larger framework that I am interested in of not - - well, I am interested in how the thing operates within the system.
Q. Yes. But my question is directed to your knowledge, quite apart from your intent in acquiring that knowledge.
A. No. That is my knowledge, the knowledge of the

A. That would be this CFCB, period.

Q. The Type 200 paper of 3 M?

A. Right.

Q. Does Moore have a self-contained paper?

A. Not commercial.

Q. Are you working on one?

MR. AMES: If this is a trade secret - -

A. Among other things, yes.

Q. Have you gotten close enough to the bench work to appreciate that that is a more difficult product to make than the transfer type paper, the CFCB Type? 12

A. No.

Q. You couldn't help us on whether it is or isn't a more difficult one to make as a practical matter? 12.1 13

A. Well, you see, once again I have to put it against the larger framework that I am interested in of not - - well, I am interested in how the thing operates within the system.

Q. Yes. But my question is directed to your knowledge, quite apart from your intent in acquiring that knowledge.

A. No. That is my knowledge, the knowledge of the

IN THE UNITED STATES DISTRICT COURT
FOR THE WESTERN DISTRICT OF NEW YORK

MOORE BUSINESS FORMS, INC., Plaintiff, v. MINNESOTA MINING AND MANUFACTURING COMPANY, Defendant.	)	Civil Action No. CIV 1972-47

AFFIDAVIT OF WALDO G. BRETSON
IN SUPPORT OF DEFENDANT'S
MOTION FOR STAY OF DISCOVERY

STATE OF MINNESOTA)
) ss.
COUNTY OF RAMSEY)

WALDO G. BRETSON, being first duly sworn, deposes and states as follows:

1. I am General Manager of the Paper Products Division of defendant, Minnesota Mining and Manufacturing Company (3M), and have held that position since the inception of that division in 1962.

2. I have read plaintiff's Interrogatories Nos. 39-48 to defendant under Rule 33 F.R.Civ.P., which seek to elicit detailed information in respect to each of 3M's facilities for manufacturing microcapsules for use in its carbonless papers, located in Nekoosa, Wisconsin; Decatur, Alabama; Cordova, Illinois; Hartford City, Indiana, and elsewhere, including:

"all improvements, modifications or other changes made" subsequent to acquisition by 3M;

"an inventory of the plant";

"a complete description of the structure of all buildings";

"all documents, including plans, drawings, reports, surveys, inventory lists, memoranda and evaluations" with respect to the facility.

3. I have read plaintiff's Motion Under Rule 37(a), F.R.Civ.P. for Order Compelling Answers to Interrogatories; and also plaintiff's Motion to Free Certain Documents from Stipulation of Non-Disclosure, wherein plaintiff seeks to have unrestricted use of documents previously shown to its counsel and bearing the identification numbers 00001-00466.

4. I have read the Affidavit of Stanley G. DeLaHunt in support of defendant's Motion for Stay of Discovery sworn to June 29, 1973, reciting various other requests of plaintiff's counsel for technological data.

5. On June 6-8, 1973, plaintiff took my deposition in this action, and also the deposition of Dr. Dean A. Ostlie. In those depositions, information was provided to plaintiff concerning its microcapsules, the processes involved in making the same, and in making products therewith. I understand that such information, and other information which has been developed in this action, forms the basis for a motion by defendant for a summary judgment of non-infringement.

6. Through sales by 3M of its carbonless paper products to plaintiff Moore, extending over a decade, I have been aware that, since at least as early as 1963, Moore has had extensive research and development programs in existence with an objective to develop products in competition with 3M's carbonless papers. I am informed that discovery in this case reveals Moore's research projects to develop carbonless paper products go back as far as 1955. Nonetheless, it was not until the year 1972 that plaintiff Moore announced a carbonless paper product to the trade, namely, "MCP" paper (standing for Moore Carbonless Paper), of its own manufacture. In this connection, I attach as Exhibit 1 hereto a copy of Moore's announcement, marked as defendant's Yeh Dep. Exhibit 8 during the deposition of plaintiff Moore's employee, Mr. Chien J. Yeh, taken by defendant in April, 1973.

7. Over the past several months, I have received numerous reports from the field that plaintiff Moore is having serious quality problems with its "MC?" paper.

8. The information which plaintiff seeks is maintained in confidence by defendant 3M. It is regarded by me as General Manager of the Paper Products Division of 3M to be highly valuable confidential technological information in the nature of trade secrets. The information contains not only secret processing data, but cost evaluation and equipment inventories, which information was developed by 3M at the cost of hundreds of thousands of dollars or more. The divulgation of such information, in my opinion, especially to an avowed competitor of 3M with products with which plaintiff is experiencing quality difficulties, would result in serious damage to defendant. The damage, in my opinion, would be great, but I would not know how its extent could be measured.

Further affiant sayeth not.

Waldo G. Bretson

Subscribed and sworn to before
me this 29th day of June, 1973.

Ruth E. Johnson
Notary Public

RUTH E. JOHNSON
NOTARY PUBLIC-MINNESOTA
RAMSEY COUNTY
My Commission Expires Feb. 3, 1980

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sales bulletin!

(copies: Specialists, Area Mgrs., & D. Winn) to All Sales Representatives
Sanda Macdonald sent this in along with samples of MCP--Lab is now testing.
date April 30, 1972
bulletin no. 46
J. Thompson

MOORE CARBONLESS PAPER

M.C.P.1 HAS ARRIVED! We are pleased to announce that limited quantities of the first of a Moore family of carbonless papers are being shipped to selected Central Division plants (Monroe and Fremont).

M.C.P. is immediately available for print orders sold from the Limited Standard Speediflo list, Classification 15, Section 3. Revised price list pages showing upcharges for M.C.P. are attached.

Paper available in white only.

Manifolding - 4 part on high speed printers.

(Other subject to customer test and acceptance)

Available price list quantities only.

(No estimates, no concessions)

Delivery starting mid June.

D.H. Yost For Ident
Exhibit No. 8 In Evidence
Date 4/12/73 J.E. Crosby

The paper being produced now, has proven that the Moore carbonless paper chemistry is capable of achieving the objectives of improved manifolding, sharp image contrast, permanency of copy, and trouble-free performance through Moore's printing presses. Complete achievement of these goals will be reached only as experience is gained in increased volume production of paper and refinements in the manufacturing process.

This is the first of a family of Moore carbonless papers that in the future will provide the Moore Sales representative with another selling advantage of competition. M.C.P. has sharper image definition than other carbonless papers, has been customer tested with proven performance through printers and after forms handling operations.

Sell M.C.P. now, from a bonus list, at a level where carbonless paper was not available previously. Sales of M.C.P.1 in large tonnage will help expedite the advance of our program to develop successor family members providing the ultimate in manifolding capability. With increased volume M.C.P. will be expanded to include colored papers, and availability in other lists and products.

This is Moore's own product, and offers great new market opportunities, in keeping with the ecology trend on waste disposal. Take full advantage of this valuable addition to your sales proposition. Make M.C.P. a part of your selling proposals. Demonstration forms and printed samples are being shipped to each district office.

MANAGER SALES OPERATING SERVICES.